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On the cover: "Mauritzite" (iron saponite) specimen collected in 2009 in the Hubertus Quarry at Erdőbénye, Hungary (type locality). Diameter of the fibres: 100 μm. Microphotograph by Erzsébet Tóth.

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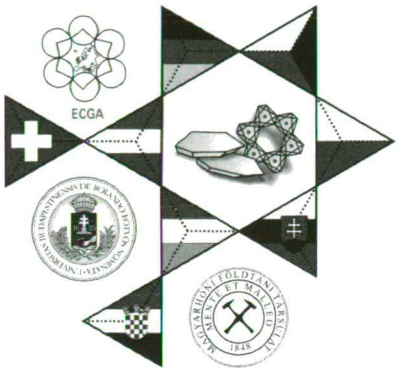

ABSTRACTS

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Luminiţa Zaharia, Annamária Kis, Boglárka Topa, Gábor Papp, Tamás G. Weiszburg

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Mineralogical co-evolution of the geosphere and biosphere

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The mineralogy of terrestrial planets evolves as a consequence of varied physical, chemical and biological processes [1]. Initial evolutionary stages include the transition from ~12 nano-scale mineral phases in pre-stellar dense molecular clouds, to ~60 primary chondrite minerals, to ~250 different minerals in altered chondrites, achondrites and differentiated asteroids. Earth's subsequent prebiotic mineral evolution depended on a sequence of geochemical and petrologic processes, including volcanism and degassing, fractional crystallization, crystal settling, assimilation reactions, regional and contact metamorphism, plate tectonics and associated large-scale fluid-rock interactions. These processes resulted in perhaps 1500 different mineral species.

Biological processes began to affect Earth's surface mineralogy by the Eoarchean, when large-scale surface mineral deposits, including carbonates and banded iron formations, were precipitated under the influences of changing atmospheric and ocean chemistry. The Paleoproterozoic "Great Oxidation Event" and Neoproterozoic increases in atmospheric O_2 transformed Earth's surface mineralogy and are responsible, directly or indirectly, for most of Earth's 4300 known mineral species.

Mineral evolution arises from three primary mechanisms: (1) progressive separation and concentration of elements from their original relatively uniform distribution; (2) an increase in range of intensive variables such as pressure, temperature, and the activities of H_2O, CO_2 and O_2; and (3) generation of far-from-equilibrium conditions by living systems. The sequential evolution of Earth's mineralogy from chondritic simplicity to Phanerozoic complexity introduces the dimension of geologic time to mineralogy and thus provides a dynamic alternate approach to framing the mineral sciences.

[1] Hazen, R.M. et al. (2008) *Am. Mineral.*, **93**, 1693-1720.

The mineral-microbe interface and its defining role in controlling contaminant mobility in the subsurface

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Recent advances in mineralogy and microbiology have led to a molecular-scale understanding of the critical role of the mineral-microbe interface in controlling contaminant mobility in the subsurface. Of particular note are respiratory processes, mediated by specialist bacteria and archaea, and coupled directly to the redox transformations of minerals. These effectively control the mobility of both inorganic and organic species in a wide range of environments and, if harnessed, may offer the basis of a wide range of innovative biotechnological processes. These applications include the bioremediation of metal contaminated land and water, the oxidation of xenobiotics under anaerobic conditions, metal recovery in combination with the formation of novel functional bionanominerals, and even the generation of electricity from anoxic sediments. Under certain conditions, however, microbial redox transformations of minerals can also mobilise toxic metals and metalloids with potentially calamitous effects on human health.

Focusing on "dissimilatory" mineral reduction processes, I will discuss recent advances in the understanding of the mechanisms of anoxic Fe redox cycling in the subsurface, and the impact of Fe mineral biotransformations on sediment biogeochemistry and the mobility of trace metals, metalloids and radionuclides. The biotechnological application of mineral-transforming metal-reducing bacteria for the generation of commercially useful bionanominerals will also be discussed, alongside their use in a range of innovative ex situ applications. The dramatic impact of advanced imaging, synchrotron spectroscopy and genomics-enabled techniques in dissecting the mineral-microbe interface will be highlighted alongside current challenges in this rapidly developing area of multidisciplinary science.

40 years of nanomineralogy

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The warm feelings conveyed by Figure 1 reflect the substantial progress that has occurred in the study of crystalline materials, including minerals, during the last four decades. That figure, lacking the Valentine Day embellishments, appeared 30 years ago. It followed developments that transformed transmission electron microscopy from a technique used primarily by biologists to one routinely utilized by solid-state scientists, including mineralogists. The changes became possible through the availability of new, highly stable microscopes for producing high-resolution images and new theory for interpreting the results. This combination facilitated the study of defects and other irregularities in crystalline and, eventually, non-crystalline solids. Additional developments continue to this day.

Fig. 1: Slightly edited HRTEM image of defects in biopyriboles; modified (by Sue Selkirk) from Fig. 1c in Veblen and Buseck [1].

High-resolution images of solids allowed the first direct visualization of structural irregularities in crystals. One no longer had to infer the crystal defects that permitted solid-state reactions to occur. Instead, it became possible to actually observe the reaction pathways through transitions and reactions "frozen" before completion. Such new information helped reconstruct processes that previously could only be inferred.

Transmission electron microscopes (TEMs) can be used to measure the crystalline structures and compositions of minerals at the micrometer to sub-nanometer scale. For particles, such as occur in the atmosphere and comprise an area of increasing interest for mineralogists, they can also be used to determine their sizes, 2D and 3D shapes, intergrowths, and coatings, all of which are of interest for atmospheric and climate studies.

The various nanoscale modes of modern TEMs include high-resolution imaging (HRTEM); energy-dispersive X-ray spectrometry (EDS) to determine compositions of inorganic species; electron energy-loss spectrometry (EELS) to measure the abundances of elements heavier than Li, their oxidation states, and chemical speciation; energy-filtered TEM (EFTEM) to show the distributions of elements within substances; selected-area electron diffraction (SAED) to determine crystallographic structures; environmental-TEM (ETEM) to measure hygroscopic properties, volatilities, and reactions at high temperature; electron holography (EH) for magnetic studies; and electron tomography (ET) to determine 3D shapes.

Mineral studies at elevated temperatures are almost routine, and we are currently trying to develop the use of TEMs to study minerals at high pressure. Examples will be provided of a range of problems addressed by studying minerals on a level ranging down to the nanoscale.

[1] Veblen, D.R. & Buseck, P.R. (1980) *Am. Mineral.*, **65**, 599-623.

Composition and evolution of the SCLM, and the origin of its diamonds

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Recent developments in seismic tomography and the integrated modeling of geophysical and petrological data have stimulated a major re-evaluation of the original composition and present extent of Archean subcontinental lithospheric mantle (A-SCLM). Analyses of seismic and gravity data, and consideration of relationships in exposed Archean peridotite massifs, suggest that the primitive A-SCLM probably was a highly depleted, moderately oxidised dunite-harzburgite, formed by high-degree melting at high T and P. Seismic tomography of cratons at regional and local scales shows "knobs" of high-Vs material that can be modeled as primitive A-SCLM, surrounded by zones of lower Vs. Kimberlites preferentially intrude these low-Vs belts, bringing up xenolith suites dominated by garnet lherzolites. By analogy with Archean peridotite massifs, these less-depleted rocks are interpreted as the result of metasomatic refertilisation, with progressive addition of cpx and garnet, and lowering of Mg#, in the peridotites. Within individual kimberlite fields, there is a direct correlation between this refertilisation process and the presence of diamonds of the peridotitic paragenesis [1]. A strong correlation between subcalcic garnets and diamonds suggests a model in which diamonds are deposited as CH_4-rich fluids are oxidized by the SCLM, producing carbonate-rich, hydrous fluids.

EMP and FTIR analyses of μm-sized fluid inclusions in "fibrous" diamonds have identified a more complex suite of high-density fluids (HDF), ranging from carbonatitic melts to "hydrosilicic" fluids and super-saline brines. LAM-ICPMS analysis of such diamonds [2] yields trace-element patterns similar to kimberlites and carbonatites, with high LREE/HREE, and high contents of alkali elements (Na, K, Rb, Cs, Ba) and HFSE (Ti, Zr, Nb...). Within single localities, carbonatitic, hydro-silicic and saline fluids have broadly similar trace-element patterns. The different types of HDF may reflect complex interactions between low-volume (mostly carbonatitic) melts, saline brines and different wall rocks (peridotitic vs eclogitic, refractory vs metasomatised).

In contrast to the fibrous diamonds, most monocrystalline diamonds have REE patterns that are either are essentially flat, or are depleted in LREE relative to HREE. They also are depleted in the alkali elements relative to the LREE, and many show strong negative anomalies in Y and Sr. These fluids and those that form fibrous diamonds may be related through carbonate/silicate melt immiscibility; the transition between them has been observed in single stones. In the Diavik mines, some monocrystalline diamonds and their fibrous/granular coats appear to have grown from the same type(s) of fluid.

If most peridotitic diamonds are related to the metasomatic modification of the dunitic Archean SCLM, then progressive metasomatism of the SCLM through time should decrease its overall prospectivity for diamonds. However, in tectonothermally younger terrains, diamonds are commonly hosted primarily in eclogites. In the absence of oxidized dunites, these mafic rocks may provide the redox environment required to deposit diamonds. Metasomatism is an ongoing process, and it is not obvious that diamonds necessarily are ancient; some may be quite „modern."

[1] Malkovets, V. et al. (2007) *Geology*, **35**, 339-342. [2] Rege, S. et al. (2005) *J. Anal. Atom. Spectrom.*, **20**, 601-611.

Mineralogical and glass compositional variations during the 2010 eruption of Eyjafjallajökull, Iceland

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After three months of magma injection beneath Eyjafjallajökull volcano, and corresponding inflation of the volcano, a lateral eruption started March 20 at the Fimmvörðuháls pass. Relatively primitive olivine and plagioclase bearing basalt was produced from ca. 500 m long fissure. After the first two days, the activity was concentrated in a single strombolian crater until March 31 when a new eruption fissure opened orthogonal to the first one. Last lava-forming activity was observed March 12. The basalt composition has a restricted whole-rock compositional range (8-9% MgO) from 3% Hy-normative at the beginning to 3% Ne-normative composition at the end. The euhedral phenocrysts assemblage is composed of Cr-rich spinel (picotite), olivine in the range Fo79-71 (with four crystals of Fo86), and a bytownite plagioclase (An81-76). Abundant vesicules and microlites characterize the groundmass, suggesting degassing-related crystallization. The interstitial glass composition is similar to the evolved FeTi-basalts of the neighbouring Katla volcano (MgO: 4.5-5.0%). During the historical period Katla has erupted twice per century; it last erupted in 1918.

On April 14 an explosive summit eruption started beneath an ice-cap with an eruption column occasionally rising as high as 8-10 km. Very fine-grained tephra of trachy-andesitic composition was produced and dispersed to the east and later to the south covering the neighbouring area with a few cm thick tephra layer. Finest part of this tephra was ejected to significant heights in the atmosphere where it sojourned for several days, and was brought over continental Europe by prevailing northeast wind directions. The fine grain-size of the tephra is not only due to rapid quenching caused by ice-magma interaction but also by fragmentation caused by rapid strain of a relatively viscous melt. The trachy-andesite produced during the first five days result from a binary mixing between fractionated basalt (similar in composition to those of Katla volcano) and a dacitic melt, possibly left-over from the penultimate eruption at Eyjafjallajökull (the 1821 dacite), and a consequent rapid magma ascent. The magma mixing is reflected by linear correlations on element-element plots between major- and trace-element concentrations obtained on whole-rock samples and in-situ by EMPA and LA-ICP-MS methods applied to primitive melt-inclusions, groundmass glasses and tephra fragments from the 1821 eruption. Three glass types are observed in the early tephra with SiO_2 concentrations of 49-51%, 60-61% and 69-70% that illustrates a mechanical magma mingling without enough time for homogenization before eruption. This results in complex mineralogical zonation with Fo64-50, An69-9 and Mg-number of clinopyroxene in the range 72-26. On May 4 a deep seismic swarm (over 20 km deep) occurred with consequent higher magma output as measured from the height of the May 5 eruption column. The tephra produced that day is comprised of well-mixed glass with SiO_2 of 62-63% but has 50μm zoned-olivines with 10 μm tick rim of Fo_{48-50}. The core has Fo_{80}, a composition similar to the olivines of the Fimmvörðuháls basalts. These results indicate a direct link between the arrival of primitive basalts, deep seismicity, increased magma pressure in the plumbing system, and higher magma output rate. Taken together, the explosive phase of the 2010 Eyjafjallajökull eruption was caused by dynamic magma mixing of mantle-derived basalt with older silicic intrusion remobilized by the crystallizing primitive basalt.

Toward theoretical mineralogy: the bond-topological basis of structure stability and mineral energetics

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The electronic properties of the constituent atoms of a structure may be represented as the diagonal elements of a square matrix, and the interactions between these atoms may be represented by the off-diagonal terms of this matrix. The form of this matrix is identical to that of the adjacency matrix of the weighted chromatic digraph of the bond network. The electronic energy density-of-states can be derived using the method of moments [1], where the trace of the diagonalized Hamiltonian matrix (of the usual secular determinant equation) has a topological interpretation in terms of closed paths in the graph of the constituent orbitals. The energy difference between two structures depends primarily on the first few disparate moments of their respective energy density-of-states [2]. Consider what this means: (1) zero-order moments are >walks in place= and define chemical composition; (2) second-order moments define coordination number; (3) fourth- and sixth-order moments define local connectivity of coordination polyhedra; energy differences between structures are dependent on these features. Open-system behaviour changes zero-order moments, closed system behaviour does not change zero-order moments. Within this framework, we may divide mineral reactions into two types: (1) those where bond topology is conserved; (2) those where bond topology is not conserved. *Conservation of Bond Topology:* The edge set of the digraph is conserved but the weights may vary depending on local changes in the vertex set. Thus the energetically most important changes involve variation in patterns of Short-Range Order (SRO). In order to conserve bond topology with varying T and P, thermal expansion and elastic compression must be accompanied by element substitutions that accord with the short-range version [3] of the valence-sum rule of bond-valence theory [4]. Thus variation in SRO is an integral part of continuous mineral reactions and drives compositional change. *Non-conservation of Bond Topology*: In a closed system, zero moments are fixed and the lowest-order changes involve second-order moments, *i.e.*, changes in coordination number. Many reactions of geological interest involve conservation of cation-coordination number, and such reactions are driven primarily by changes in anion-coordination number. The correspondence principle of Lewis acidity – Lewis basicity [5] may be used to explain the structural and chemical complexity of many surficial minerals. Where data are available, species in aqueous solution follow the valence-sum rule, and their Lewis basicities scale with the pH values of the solution at maximum abundance of the species in solution. The complex species in aqueous solution actually form the building blocks of the crystallizing minerals, and in principle, the structures thus retain a record of the pH of the nascent solutions from which they crystallized. This general approach has an atomistic basis and yet is sufficiently simple that complex problems can be addressed in a transparent yet quantitative manner.

[1] Burdett, J.K. et al. (1984) *Croatia Chem. Acta*, **57**, 1193-1216. [2] Burdett, J.K. & Lee, S. (1985) *J. Am. Chem. Soc.*, **107**, 3063-3082. [3] Hawthorne, F.C. (1997) *Can. Mineral.*, **35**, 201-216. [4] Brown, I.D. (2002) *The Chemical Bond in Inorganic Chemistry. The Bond Valence Model.* Oxford University Press. [5] Hawthorne, F.C. & Schindler, M. (2008) *Z. Kristallogr.*, **223**, 41-68.

X-ray spectroscopy on geomaterials using synchrotron radiation

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In the last two decades, synchrotron radiation (SR) has become an indispensable tool for studying geomaterials using X-ray spectroscopic techniques. The continuous spectrum and the high brilliance produced by a SR source not only enable the acquisition of high quality data in short time, but also provide the possibility to focus the SR beam into small spots with very high photon flux. Particularly the latter feature is a prerequisite for many applications in Earth sciences. In this lecture, a sequence of examples using X-ray spectroscopic techniques is discussed, which highlight the versatile applicability to many materials of geological interest at the relevant geological conditions.

One very important application using the fine structure observed at the X-ray absorption edge (XANES) represents the investigation of redox processes. For Fe, the pre-edge region provides an almost direct way of quantifying the oxidation state in many crystalline and non-crystalline compounds [1], even with microscopic spatial resolution, e.g. [2]. XANES at the S K-edge may be used to study S-redox equilibria in melts, e.g. [3]. E.g., new XANES derived data show a much narrower transition from sulfide to sulfate with oxygen fugacity than previously determined with the electron microprobe. This may have considerable implications for the sulfur behaviour in subduction-related magmas [4]. Time-resolved XANES may even be used to determine the progress and mechanism of redox reactions. E.g., this was nicely shown for the case of oxidation of Mn(II) by bacteria [5].

Due to the rather low absorption of hard X-rays by matter, SR opens up the possibility to perform measurements in high-pressure or reaction cells. SR micro-XRF is used for obtaining trace element concentrations in aqueous fluids in-situ at high P and T using an XRF-optimized diamond anvil cell, with detection limits in the lower ppm range [6,7], even for low Z elements such as Ti [8]. A particular advantage over any quench technique is the possibility to study directly the kinetics of equilibration [9]. Furthermore, the high-pressure setup is used to investigate the element complexation in aqueous fluids by acquiring X-ray absorption spectra at conditions of the Earth's crust, e.g. REE in model fluid compositions [10]. XANES on Fe in hydrous melt at P & T provides evidence for non-quenchable structural re-organizations in the Fe environment during the cooling to a hydrous glass [11]. These valuable insights cannot be achieved on quenched samples at all and show the importance of these studies particularly for the understanding of processes at high P and T.

The soon dedication of new and upgraded SR sources for hard X-rays, will make sure that the conditions for such studies will improve and will certainly open up possibilities for new experiments to provide access to parameters not accessible so far.

[1] Wilke, M. et al. (2001) *Am. Mineral.*, **86**, 714-730. [2] Schmid, R. et al. (2003) *Lithos*, **70**, 381-392. [3] Wilke, M. et al. (2008) *Am. Mineral.*, **93**, 235-240. [4] Jugo, P.J. et al. (2010) *Geophys. Res. Abstr.*, **12**, EGU2010-7075. [5] Bargar, J.R. et al. (2000) *Geochim. Cosmochim. Ac.*, **64**, 2775-2778. [6] Schmidt, C. & Rickers, K. (2003) *Am. Mineral.*, **88**, 288-292 [7] Schmidt, C. et al. (2007) Lithos, **95**, 87-102, [8] Manning, C.E. et al. (2008) *Earth Planet. Sci. Lett.*, **272**, 730-737. [9] Borchert, M. et al. (2009) *Chem. Geol.*, **259**, 39-47. [10] Mayanovic, R.A. et al. (2009) *Chem. Geol.*, **259**, 30-38. [11] Wilke, M. et al. (2006) *Chem. Geol.*, **229**, 144-161.

Phosphate mineral reactivity: from nano to global scales

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Life as we know it on Earth needs phosphate for its many biological roles, for example as the backbone of DNA. As a result, phosphorus availability often regulates biological productivity in many terrestrial and marine environments, but when in excess, leads to uncontrollable biological growth linked to water quality problems (eutrophication).

Phosphate minerals have a central role in this process, as they are the "gatekeepers", sources and sinks, of phosphorus in environmental and biological systems. Phosphate mineral solubility is particularly relevant, but exceptionally complex, notably in the case of apatite, the most common and perhaps most important of all phosphate minerals.

An important aspect of the phosphorus global cycle is that its only primary source is phosphate ore, which is a finite resource, with some predictions suggesting there remain as little as 125 years worth of global reserves. If phosphorus is no longer available or becomes too expensive, major consequences on global food production can be expected. It is therefore essential that the use of phosphorus be reviewed and potentially regulated.

Apatite in its various forms as a biological or chemical precipitate will form the focus of this paper. Its dissolution and precipitation kinetics and the influence of organic species in these processes will be reviewed and our efforts to understand its reactivity within environmental and biological matrices will be discussed. These processes, happening at the nano scale, could potentially have global consequences.

The nuclear fuel cycle: role of mineralogy and geochemistry in the safe management of nuclear waste

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During the past five years, there has been a renewed interest in nuclear power as a source of energy that does not emit green house gases. An important consideration remains the environmental impacts of mining uranium and the final disposition of nuclear wastes. In addition, advanced nuclear fuel cycles, which involve new reactor types and reprocessing of used fuel, will require the development of new materials and create new waste streams.

In parallel with this renewed interest in nuclear power, the Office of Science of the U.S. Department of Energy has conducted a series of *Research Needs* workshops that have outlined cutting-edge research areas that will be required in order to support the nuclear "renaissance". Two of the reports, *Basic Research Needs for Advanced Nuclear Energy Systems* and *Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems* outline a research agenda for mineralogists and geochemists involved in both the "front-end" and "back-end" of the nuclear fuel cycle. A third report, *Basic Research Needs for Materials Under Extreme Environments* outlines a research agenda that has important overlaps with the research of the mineral physics community. The research agenda are organized according to:

- immediate research needs,
- "use-inspired" basic research,
- cross-cutting fundamental research,
- grand challenges

Typical of the scientific Grand Challenges are: *i.*) physics and chemistry of actinide-bearing materials; *ii.*) first principles, multi-scale modeling of complex materials under extreme conditions; *iii.*) the design of molecular systems for chemical selectivity during processing.

I will identify the relevant areas of research for mineralogists and geochemists with examples from:

- the design and properties of nuclear waste forms;
- corrosion of spent nuclear fuel;
- radiation effects under extreme conditions.

Zircon – more than just a chronometer

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Zircon ($ZrSiO_4$) is a mineral of singular importance in Earth Science. Based on its robust retention of formation ages and its ability to substitute a wide variety of trace elements that record the conditions of its formation or alteration, zircon has become the foremost among our geochronometers. No other mineral has the capability to help us unravel so much about how our Earth has evolved chemically and structurally through time. In addition, zircon is continually revealing how broad its capacity is to record the timing of events that have occurred across a vast range of geologic environments from the upper mantle through to the near surface environment. The rock types and environments in which we find zircon seems only limited by our curiosity to look.

The use of zircon for U-Pb dating by isotope dilution or microbeam methods has become almost routine, supported by continued advances in our ability to analyse smaller and smaller sample volumes at higher and higher analytical precision. However, it is the ability to directly link geochemical signatures with absolute time constraints that makes zircon such a powerful tool to be brought to bear on any number of geologic problems. For example it is now commonplace to integrate U-Pb zircon ages with Hf isotopes to fingerprint the sources of magmatic rocks; O isotopes to evaluate the contribution of mantle melts to crustal magmas as well as the role of high- vs low-temperature processes in the environment of zircon growth or alteration. The rare earth and other trace elements are commonly used to trace the environments of zircon growth be they high-temperature and in the presence of melts or during hydrothermal fluid events. The addition of Ti to this arsenal of geochemical tracers has now given us the ability to place direct temperature estimates on zircon growth. Moreover, U-Pb dating is now being integrated with U-Th/He methods thereby providing us with valuable information about exhumation in mountain belts and the coupled depositional histories of the detritus eroded from these mountains.

In the coming years research will address our incomplete understanding of the true complexity recorded at the micro-scale in zircon and what part of a geologic history fragments of a single zircon may represent. This work will hopefully enhance our ability to interpret the mechanisms that lead to zircon growth and modification, not only improving the meaning of zircon ages but also giving us robust means with which to use such fine-scale features to describe the intricacies in geologic processes that individual zircon grains bore witness. Such advances will continue to emphasise the importance of this tiny, but timely, mineral.

Biomineral attractions: magnets in organisms

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Many organisms contain ferrimagnetic nanocrystals. Bacteria, pigeons and fish are known to use magnets for navigating in the Earth's magnetic field, whereas some animals use the iron minerals for hardening or protection. However, in most cases the biological functions of magnetic crystals remain unknown.

Magnetotactic bacteria are the best known examples of organisms that contain nanoscale magnets. Specific strains of bacteria form magnetite (Fe_3O_4) or greigite (Fe_3S_4) crystals, or both, in their cells. The membrane-bound, ferrimagnetic nanocrystals (magnetosomes) have species-specific sizes and morphologies and various arrangements, most often in linear chains. Cells of magnetotactic bacteria provide a natural laboratory, in which the magnetic properties of nanometer-sized particles can be studied.

We have used a combination of advanced transmission electron microscopy techniques, including off-axis electron holography, to study the structural, magnetic and chemical properties of magnetic nanocrystals inside magnetotactic bacteria. The samples studied included uncultured magnetotactic cells collected from both marine and freshwater environments, and cultures of the strain *Magnetospirillum gryphiswaldense* and its genetically-modified mutants.

We studied the fine details of magnetic induction maps determined from electron holograms obtained from magnetosomes with a range of sizes and spacings. Based on these results, an experimental "magnetic-state phase diagram" was constructed that highlights the delicate balance between the magnetic state of a crystal, its size, shape and orientation, and the chain configuration, and illustrates graphically whether cells are able to respond effectively to the geomagnetic field. In general, the shape anisotropy of each crystal is the most important factor in controlling the magnetic microstructures of ferrimagnetic crystals in bacteria, followed by interparticle interactions and, least important, magnetocrystalline anisotropy. Despite significant variations in the magnetic properties of magnetosome chains, all of the wild-type cells had permanent magnetic dipole moments that were sufficient for magnetotaxis.

Biogenic magnets exhibit fascinating combinations of magnetic properties and biological functions. However, except for ferrimagnetic particles in magnetotactic bacteria, relatively little is known about them. Further work is needed to understand magnetic sensing in animals and the functions of magnetite particles in humans. A key challenge is the localization and preparation of tissues that contain ferrimagnetic particles. Once such samples are available, advanced analytical techniques, including off-axis electron holography, can be used to provide detailed characterization of the structures, compositions, arrangements and magnetic properties of biogenic nanomagnets.

Mechanisms of cellular and biomacromolecular interactions with minerals in humans

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Medical Mineralogy involves the mechanistic study of interactions between of cells and biomacromolecules with minerals and aqueous solutions that are of relevance to biomedical applications and human health. The unique contribution of mineralogists to the health-related fields can be to emphasize the critical contributions of structure, composition, particle size, bulk and surface chemistry of the mineral or amorphous solid phase to the thermodynamics or kinetics of the relevant reactions of interest.

I will illustrate these ideas with two example studies. The first study deals with the potential for using bioactive silicate glasses and ceramics (wollastonite, pseudowollastonite) in orthopaedic implants for bone-tissue engineering. Porous silicate implants can be seeded with human mesenchymal stem cell (hMSCs). As the implant dissolves in the body, the silicon released from silicate hydrolysis may promote the differentiation of hMSCs down the osteoblastic lineage, promoting rapid bone growth and, eventually, complete replacement of the implant by newly-formed bone. However, Si released may also be potentially cytotoxic to and reduce adhesion of the hMSCs. Additional soluble factors such as Ca and P in the ambient fluid environment may also work cooperatively or as antagonists to Si, and physical factors such as surface rougness, porosity, etc., also affect hMSC adhesion, viability, and differentiation. Thus, numerous factors must be optimized simultaneously.

In the second example, I will discuss the potential role of acidic, non-collagenous proteins (ANCPs) in controlling the nucleation and growth of hydroxyapatite in bone biomineralization. Bone is a nano-composite material of collagen matrix fibrils in strict hierarchical arrangement with nancrystals of highly non-stoichiometric, highly substituted hydroxyapatite and associated ANCPs. I report the potential role of a NCP called Bone Sialoprotein (BSP) in nucleating a calcium phosphate phase. Using Molecular Dynamics simulations, we have studied the effects of both structure (alpha-helix versus random coil) and primary amino-acid sequence (wild-type versus *in silico* mutations) of a highly-conserved acidic peptide from BSP interacting with dissolved Ca^{2+} and HPO_4^{2-} ions to form an initial calcium phosphate nucleus, and to interact with (100) and (001) faces of hydroxyapatite in modulating crystal growth.

Mineralogy and geochemistry at lower dimensionality: mineral-water interfaces and nanoparticles

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Over the last ten years experimental methods using synchrotron radiation have been developed to determine and refine the *in situ* molecular structure at mineral surfaces in analogy to that historically accomplished for bulk solids many years ago. We can thus begin to apply the rules of crystal chemistry, appropriately upgraded to include modern simulation tools, to surfaces, interfaces and grain boundaries. As surfaces are rarely precisely like the terminated bulk structure in terms of reactivity, chemistry and stoichiometry, we are thus gathering new insights into interface reactions like sorption, precipitation and acid-base equilibria [1]. These developments are timely inasmuch as nanomineralogical studies benefit markedly from an improved ability to understand the chemical characteristics of surfaces, edges and other "low coordination" surface topologies. Additionally, studies on both surfaces and nanoparticles yield information on local water structuring and hydrogen-bonding, with both being needed to completely define a nanoparticle surface and its properties [2].

Current studies include various surface-sensitive scattering and spectroscopic techniques, supported by both classical and ab initio calculations, but with almost all efforts aimed at characterizing near equilibrium or steady state interface structure. In the future, dynamic studies will be possible, with processes such as crystal growth, dissolution and even electron transfer reactions accessible on a true molecular level for the first time.

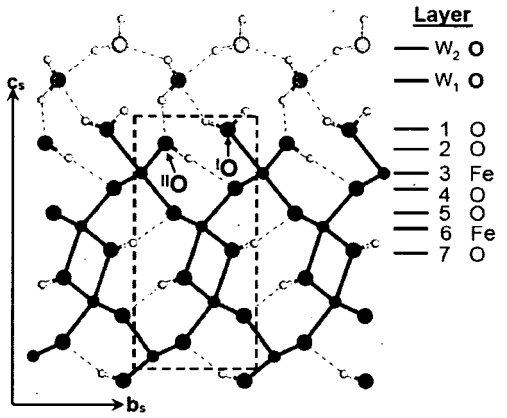

Fig. 1: Structure of the (100) cleavage face of goethite obtained from surface x-ray scattering showing surface bound functional groups (FeOH, $FeOH_2$) and two layers of ordered water [3]. The surface oxygens in Layer 1 and 2 are relaxed from their positions in the bulk structure. Dashed lines indicate likely hydrogen bonds.

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The active surface of clays for healthy environments: dynamic of pesticides

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Clays and "anionic clays" are layered natural and synthetic compounds, respectively, with very special surface properties. They are wonderful materials!

Clay minerals are composed by aluminosilicate layers negatively charged balanced with cations in the interlayer space. Smectites are a clay mineral group having swelling or expandable structure that makes the interlamellar structure accessible to cationic or polar organic molecules. On the contrary the "anionic clays" are layered double hydroxides (LDH) positively charged that is balanced by hydrated anions between the layers. Moreover, LDH has a very special property: when heated at 500ºC a mixed oxide is obtained and when put it in water rehydrates, recovering the original LDH structure. The sorption of anions from aqueous solutions by reconstruction of LDH structure is based on so-called "memory effect", which provides them with recycling possibilities. Several examples of interactions of these materials and organic molecules are shown.

The main characteristic of these materials is the high adsorption capacity and how easy they can be modified by changing the original surface properties into new ones almost "a la carte". The layer charge and the origin of the charge is a key parameter affecting sorption and chemical and phothochemical degradation reactions.

Clay minerals and LDHs are important sorbents when chemicals are ionic, ionizable or polar because their hydrophilic character. Replacement of inorganic interlayer exchangeable ions by organic ones has been shown to change the nature of the surface from hydrophilic to hydrophobic increasing mineral affinity for hydrophobic organic compounds. The selective modification of clay minerals with organic cations containing appropriate functional groups is a novel technique to maximize the affinity of the adsorbent for a given chemical.

These organoclays can be widely used as sorbents for diverse target molecules. These materials are of special interest for decontamination or contamination prevention purposes in soil and water environments e.g: in clay-pesticide formulations. Factors influencing the release rate and extent of pesticides from clays and organoclays are still issues which need to be addressed. The characteristics of the clay mineral, the amount and nature of exchangeable cations, the clay-pesticide ratio, and the procedure followed to prepare the formulation all affect the interaction of the pesticide with the sorbent and in turn its release from the formulation. Interactions mechanisms of original and modified clays with organic molecules are discussed.

Organoclays and organoLDHs based on large and small organic cations/anions are proposed not only as carriers in pesticide formulations to retard pesticide leaching after soil application and slow release of bioactive chemicals and photostabilizers but also as filters or barriers for water decontamination.

Uptake of uranium(VI) by clay minerals

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The transport of U(VI) in columns packed with different clay minerals was investigated. The major aim was to verify if the phenomena reported in previous batch experiments are true as well with flow through conditions.

Although smectites have higher cation exchange capacity than kaolinites, both kaolinite minerals (KGa-1b and KGa-2) showed much greater uranium sorption than smectites; requiring hundreds of pore volumes to achieve breakthrough. This can be considering as obvious evidence that surface complexation was the dominant mechanism for uranium retardation in all columns. The high uranium sorption capability for kaolinite is because it contains more exposed aluminol surface site which have greater binding affinity with respect to uranium than silanol sites.

The irreversible sorption of U(VI) observed in smectites packed columns can be attributed to the high content of iron oxide in the bentonite structure (e.g, 4.3% for SWy-2) comparing to that in the kaolinite structure (e.g., 0.2% for KGa-1b), which has a pronounced sorption affinity to uranium. In addition, the presence of the basal plane in (2:1) clay minerals can obviously delay the U(VI) desorption. Therefore, a slow diffusion of uranium from the surface into the interlayer forming stable surface complexes is delaying uranium extraction. The mineral composition and the degree of crystallinity plays an important role for sorption and desorption of U(VI).

Quantitative U(VI) recovery rates were obtained from the calculation of mass balance in all columns. U(VI) was totally recovered from kaolinite (although slowly), whereas 53 µg and 93µg of U(VI) remains in STx-1b and SWy-2 at the end of the experiments, which is an clear indication for irreversible adsorption (Table 1).

On the contrary, it is noticeable that the amount of U(VI) desorbed from IBECO was significantly higher than sorbed before. This can be attributed to an amount of uranium released from bentonite structure.

Table 1: Mass balance for sorbed and desorbed uranium

	Total U in µg/L	
Columns packed with	**sorbed**	**desorbed**
IBECO	474	542.1
STx-1b	566	513
SWy-2	724	631
KGa1b	877	877
KGa-2	939	928

A fast method to determine the cation exchange capacity of clays with guanidinium

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The common procedures of determining the cation exchange capacity (CEC) of clays with ammonium ions are often time-consuming and laborious [1]. Fast methods have been developed for a wide range of clay minerals using transition metal ions as exchanging index cations, e.g. copper triethylenetetramine $[Cu(trien)_3]^{2+}$ [2]. However, this method suffers from a significant underestimation of the CEC of vermiculite-bearing soils. The values depend from sample preparation. Excessive mechanical and chemical pretreatment and a longer exchange reaction time are needed to measure vermiculite CEC values effectively [3].

A new method was developed to measure the CEC of vermiculites in a simple way by exchanging the cations in one step by the highly adsorbing organic cation guainidinium $C(NH_2)_3^+$. Guanidinium (Gdn) concentrations were measured by fluorescence spectroscopy following a method proposed by Conn and Davis [4].

In our approach only some simple mechanical sample preparation is required before the exchange reaction. The sample material needs to be grinded down to a grain size less than 63 µm. Dispersion in water is achieved by ultrasonic treatment prior to the addition of the index ions. The exchange reaction then takes place within 4 hours in an aqueous solution of guanidine hydrochloride. Table 1 gives a comparison of the CEC obtained by different methods for a bentonite and a vermiculite.

Table 1: CEC (meq/100 g) from different methods

	(1)	(2)	(3)
Bentonite Calcigel	65	65	64
Vermiculite <63 µm	159	25	150

(1) Ammonium method [1], (2) Cu(II)trien method [2]. (3) Gdn method

First results show good agreement of the CEC measured with guanidinium and those measured with ammonium. Currently an experimental program is running, to apply the method to a larger range of clay minerals and to determine and improve the accuracy and the precision of the method.

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Investigation of adsorption properties of a kaolinite and nontronite containing clay from Dikozu region (Eskisehir-Turkey)

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Instrumental characterization of a clay sample from Dikozu region (Eskisehir-Turkey) was performed by various techniques such as XRD, XRF, TGA/DTA, SEM. XRD analysis was realized by XRD apparatus (Rigaku, Rint 2200). Weight percentages of the sample were calculated from XRD pattern via the method developed by Moore and Reynolds [1] (Table 1). Besides, IR spectrum of the sample was obtained from FTIR spectrometer (Bruker, IFS 66v/S). Chemical analyses of the sample were taken by means of an WDXRF apparatus (Rigaku, ZSX Primus) (Table 1). TGA/DTA analysis of the sample was obtained from Thermal Analysis System (Setaram Setys Evolution 1750) and SEM images were taken by SEM system (Zeiss, EVO 50 EP). The results of instrumental analyses were compared with each other and they show consistency [2,3].

Table 1: XRD and XRF results of the sample from Dikozu region (Eskisehir-Turkey)

Components of the clay sample: nontronite (20.1%), dolomite (35.1%), kaolinite (44.8%)
Chemical analysis of the clay sample: SiO_2(49.183%), Al_2O_3(29.35%), Fe_2O_3 (2.654%), K_2O(0.043%), MgO(8,571%), TiO_2(0.08%), other (0.814%), ignition loss (23.516%)

The clay sample, 90 µm in size, was prepared by grinding and sieving processes. After the preparation of the sample, the investigation of adsorption properties was realized by high speed volumetric sorption analyser (Quantachrome, Nova 2200). Before analysis of the adsorption properties, the sample was activated thermally in 110°C during 3 hours. Specific surface area and density of the sample were determined in the medium of liquid nitrogen (77K) by using B.E.T. method. Adsorption isotherms were consistent with B.E.T. model. After obtaining the B.E.T.isotherms, the values of the specific surface area and density of the sample were 53.043 m^2/g and 2.2 g/cc respectively.

Investigation of water vapour adsorption properties of the sample was realized by volumetric adsorption system (Quantachrome, Autosorp 1). Water vapour adsorption-desorption isotherms were consistent with B.E.T. model. Specific adsorbed water vapour, specific surface area and specific retention capacity of the sample were 30 cc/g 147.2 m^2/g and 32.630 cc/g respectively. The specific surface areas of the sample determined by using different adsorbates were found different. This difference comes from the molecular structures of nitrogen and water.

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Stability and forms of Fe in natural and modified clays: connection to sorption properties

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The stability and forms of structural Fe in natural aluminosilicates have been usually based on the redox potential, predominantly in aqueous environment. The oxidation-reduction processes of Fe particles in soils and sediments strongly influenced not only physical chemical properties, but also surface properties of aluminosilicates (specific surface area, surface charge) [1], closely related to the adsorption behaviour of solid phase.

Recently Fe-modified aluminosilicates have opened new possibilities in adsorption technologies due to the change of surface charge (pH_{ZPC}) and thus a strong affinity to anionic contaminants. Four natural and two modified clays with a high content of Fe (Table 1) were investigated in term of Fe forms, their changes during adsorption processes and the stability under balanced and/or disturbed conditions in solid-aqueous system (redox potential, ionic strength, pH, microbial activity, competitive ions, etc.) [2,3].

Table 1: Relative content of Fe in natural and modified clays (% wt.)

	locality	characteristic	Fe (%wt)
Kaolinite	Király Hill, Hungary	natural	3.0
Illite clay	Illite pit in Tokai, Hungary	natural	1.7
Smectite clay	Lignite pit, Visonta, Hungary	natural	to 6.9
Calcined kaolin	West Bohemia, CR (pit)	modified Fe^{2+}/Fe^{3+}	4.1/27.2
Bentonite	West Bohemia, CR (pit)	natural modified Fe^{2+}/Fe^{3+}	14.6 17.8/28.6
Kaolinite clay	West Bohemia, CR (clay deposit)	natural	8.9

The detailed characterization of Fe chemistry in different types of aluminosilicates anabled to predict the stability and detention time of surface fixed particles forming complexes and/or covalent bonds via Fe ions. These properties particularly affected the adsorption quality of clay sorbent both in natural systems and in technological processes. The adsorption/ desorption of dissolved ions including toxic contaminants strongly depended on their initial concentration, and also on surface Fe phases (their amount and chemical forms). However, the stability of saturated sorbent also related to the type and purity of clay matrix, binding character, physical chemical properties and ageing time.

Acknowledgements: This work was the part of the project P210/10/0938 (Grant Agency of Czech Republic) and the research programme MSM 6046137302 (CR).

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Synthesis and investigation of physicochemical properties of Zr,Al-pillared montmorillonites

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Nowadays for direct elimination the pollutions considerable attention has been given to the development of new functionally active sorbents based on clay minerals due to their unique structural and physicochemical properties. Multicomponent systems containing two mixed ions, such as Al/Ga-, Al/Fe-, and etc., are of particular interest due to their unique textural and physicochemical properties.

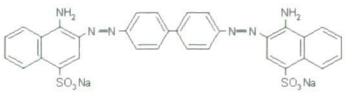
A Na-containing naturally occurring montmorillonite was intercalated with solutions containing Al-, Zr-, and mixed Zr,Al-cations, with various Zr/Al ratios [1]. The Zr,Al-PILCs were obtained by calcination of the intercalated precursors at 450°C. Characterization studies were performed by use of XRD, FTIR, DR-UV-vis and N_2-adsorption/desorption analysis.

Effect of Zr/Al ratio of Zr,Al-containing pillaring solution on structural and physicochemical properties of Zr,Al-PILCs was examined. As can be seen from Table 1 all Zr,Al-PILCs showed ordered, layered structures with basal spacing between 18.3 -16.4 Å (14.7 Å for Na-clay). The increase in Zr content in Zr,Al-PILCs favours the increase in interlay distance (d001), although the specific surface area slightly changes.

Table 1: Textural data of Zr,Al-PILCs

	Al % wt	Zr % wt	S_{BET} $m^2 \cdot g^{-1}$	d_{001} Å
Al-CAC	8.80	0	216	18.3
Zr,Al-CAC(70/10)	8.76	1.89	271	17.6
Zr,Al-CAC(70/20)	8.72	3.58	240	17.0
Zr,Al-CAC(70/30)	8.15	3.00	205	16.4
Zr-CAC	5.55	11.6	206	10.7

The increase in Zr content makes alterations in nature and strength surface functional groups that were confirmed by IR spectra of adsorbed CO and $CDCl_3$. The increase in Zr content leads to the change in surface acidity. The Zr,Al-PILC in the aqueous suspensions became coloured after the adsorption of Congo red (CR). The following stainings were obtained, on Zr,Al-PILC(10/70) - red, on Zr,Al-PILC(20/70) - violet-red and on Zr-PILC - dark violet (Fig. 1). It appears that CR can serve as an indicator of the surface acidity of montmorillonite.



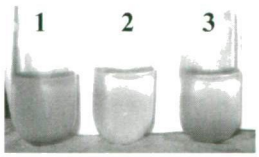


Fig. 1: Adsorption of Kongo red (0.035 $mg \cdot ml^{-1}$) on Zr,Al-PILC(10/70) (1), Zr,Al-PILC(20/70) (2) and Zr-PILC (3) at 25°C.

The effects of surface acidity of Zr,Al-PILCs, initial pH value of the Congo red dye solution and temperature on adsorption capacities of samples for CR dye have been investigated.

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Electric-field induced alignment of modified Na-fluorohectorite clay particles

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The electric field induced alignment of organically modified sodium-fluorohectorite (Na-Fh) clay particles suspended in silicone oil was studied by means of synchrotron wide angle X-ray scattering (WAXS).

This report focuses on the comparison between the anisotropic arrangement of organically modified clay particles and their previously studied non-modified counterparts [1].

Na-Fh particles suspended in oil undergo a fast and extended structuring when subjected to an electric field [2]. As a coarse approximation, the Na-Fh clay platelets forming the chain can be represented as disk-shaped aggregates, whose orientation is defined by a unit normal vector. Thus, the anisotropic arrangement of the system can be described by an orientation distribution that is a function of the normal vectors for all aggregates [3]. The classical Maier-Saupe function was used for the orientation distribution, since it was found to be suited to our data, as discussed previously by Méheust, et al. [4]

In fig. 1 the experimental set-up is presented whereas fig. 2 shows two-dimensional diffractograms.

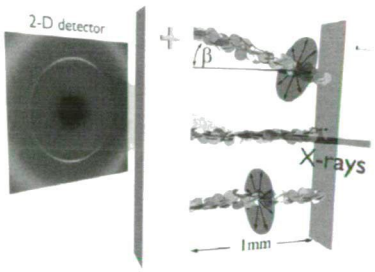

Fig. 1: Experimental geometry for the WAXS measurements. Particles are forming chains along the E-field.

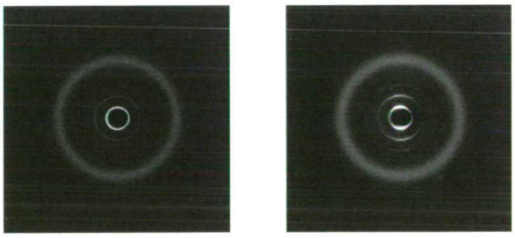

Fig. 2: WAXS patterns of modified clay particles without (left) and with (right) E-field applied (0.35 kV/mm).

The WAXS data showed that the degree of anisotropy was higher for the system with organically modified Na-Fh particles (S=0.71) than for unmodified clay particles (S=0.63). This can be explained by fact that the modified clay particles do not form large aggregates as it is the case with unmodified particles, leading to a better organization of the constituents of this electrorheological fluid.

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Dissolution of the surfactants modified montmorillonite in HCl

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Various concepts have been applied to modify the properties of clay minerals in order to widen their possible applications. For example, cationic organic surfactants are often used to change their surface properties. On the other hand, acid activation is an appropriate method for alteration of the clay minerals structure. In this work these two methods of modification are united and the stability of organo-modified montmorillonite in inorganic acid and the influence of the acid treatment on final textural and morphological properties of obtained products are examined.

Ca^{2+} cations in Ca-SAz-1 montmorillonite were exchanged with organic cations with different length of alkyl chains: tetramethylammonium (Me_4N^+), tetraethylammonium (Et_4N^+), tetrapropylammonium (Pr_4N^+), and tetrabutylammonium (Bu_4N^+). The results of the chemical analysis revealed very low Mg and/or Al content present in the solid reaction product after 8 hrs dissolution of Ca-SAz-1 in 6 M HCl, indicating almost completely decomposed sample. Me_4N-SAz sample was dissolved in similar extent. However, with increasing size of the organic cation higher resistance to acid attack in order≤Ca $Me_4N^+ < Et_4N^+ < Pr_4N^+ < Bu_4N^+$ was observed. About one half of the initial aluminium content still remained in the solid reaction product for Bu_4N-SAz dissolved even for 8 hrs. SEM analysis showed that destruction of the original layer composition upon acid treatment became evident also from the overall morphology of the particles, their size and aggregation. The exposed planes of large plate-like montmorillonite aggregates were disintegrated and smaller fine grains were created. Formation of protonated silica as a product of acid leaching led to the sharp increase in BET surface area of Ca-SAz-1 from 70 m^2/g to 467 m^2/g, after 4 hrs of treatment. The only sample reaching the similar maximal BET value was the 4 hrs treated Me_4N-SAz. The course of the BET values for all samples is given in Fig. 1. The gradual increase in the BET surface area was also observed for Bu_4N-SAz, but it did not reach the values found for other studied samples (Fig. 1), which confirmed only partial decomposition of this montmorillonite. Bulky organic cations cover larger surface area of montmorillonite, what decreases the accessibility of the interlayers to proton attack causing the increase in the resistance of the clay layers to the acid.

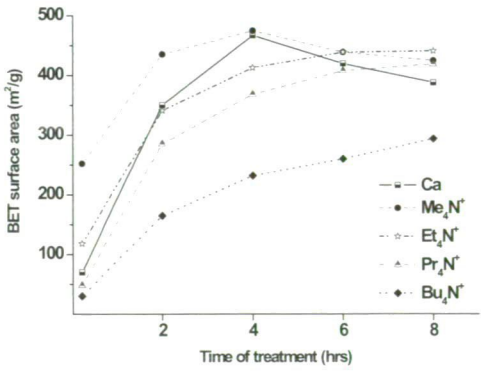

Fig. 1: BET surface areas of untreated samples and samples dissolved in 6M HCl at 80°C for various times.

Influence of clay's cation exchange capacities (CEC) on organoclay structure and locations on the loaded surfactants

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During the last two decades, organoclays have attracted great interest due to their wide applications such as adsorbents for organic pollutants and clay-based nanocomposites [1]. However, some important aspects still have not received enough attentions, such as the influence of the characteristics of the used clays and configuration of the used surfactants on the microstructure and property of the resultant organoclays, the microstructural evolution of organoclays when heated. These are of high importance for the applications of organoclays.

In this study, three montmorillonites with different cation exchange capacities (CECs) and surfactants with different alkyl chain length and chain number were used to prepare organoclays at different surfactant concentrations. A combination of various characterization techniques was applied to investigate the microstructure of the obtained organoclays and their microstructural evolution when heated. The present study shows that the basal spacing of the organoclays increased with surfactant loading [2,3], while the maximum basal spacing increased as the alkyl chain length of the surfactant increased [2]. For the same surfactant, the maximum basal spacing of the organoclays was little influenced by the CEC of the montmorillonite component [4]. The level of surfactant loading required to reach the maximum basal spacing, however, strongly depended on the CEC. For a given surfactant, the maximum basal spacing increases with the increase of chain number.

When heating the organoclays, there is a slight increase of basal spacing before 340°C and after this temperature, there is an obvious decrease of the basal spacing, indicating the degradation the intercalated surfactants. The XRD patterns at different temperatures and TG curves of the organoclays indicate that there are two basic different locations of the loaded surfactants: 1) adsorbed on the clay external surfaces, including in the pores available between clay particles with a "house of cards" structure [5], 2) intercalated into clay interlayer spaces via two different ways, i.e., surfactant cations replacing the interlayer exchangeable metals and surfactant molecules being adsorbed into interlayer spaces [6,7].

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Effect of clay amendments on wettability of peat-based growing media – relation between capillary water uptake and EDX data on surface composition

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In Europe 200.000 tones of clays are used for growing-media annually. Peat, an important substrate component gets highly hydrophobic if it is getting dry. The addition of clay to peat induces a coated surface with hydrophylic properties on the organic matter which improves rewettability and reduces the risk of erroneous irrigation. At present there is only empirical knowledge about the amount of clay needed and the optimum mineral parameters for different horticultural purposes.

For the organic substrate component a blend of different sphagnum peats with a moderate degree of decomposition, obtained from Klasmann Deilmann GmbH (Geeste-Groß Hesepe, Germany) was used. Seven clay samples highly different in their mineral parameters from the Mesozoic-Tertiary weathering mantle, Rhenish Massif were obtained from Stephan Schmidt KG (Langendernbach, Germany). A saprolitic clay, two bentonites, and two translocated clays as well as two blends were included. Mixtures of 10, 20, and 30 kg clay with 1 m^3 peat were prepared.

For the evaluation of the water uptake characteristics a capillary-rise method, developed for inhomogeneous, fibrous and swelling materials (Dutch RHP-foundation) was used. The coverage degree of the peat surfaces with clay minerals was described by the C/Si ratio determined by energy dispersive X-ray spectroscopy (Quanta 200, Fei) for sections of 6 mm^2.

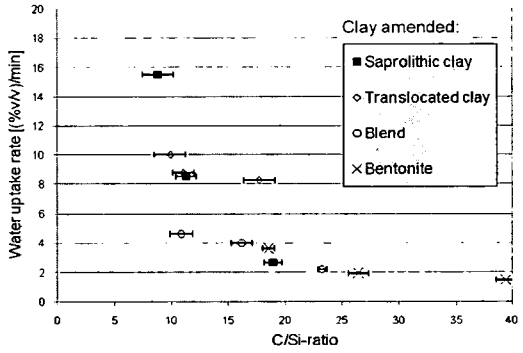

Fig. 1: Effect of four different clays amended in amounts of 10, 20, and 30 kg/m^3 peat on the water uptake rate. The C/Si ratio (n=5) indicates the coverage degree of peats surfaces with clay.

At low C/Si ratios, where the surfaces of peat are most complete coated with clay minerals, all clay-peat systems show the highest water uptake rate (Fig. 1). Highest variability is observed for a saprolitic clay rich in illite and kaolinite, where the water uptake rate ranges from 2,6 to 15,5 %v/v/min. For the translocated clay and bentonite, the absolute amount of amended clay showed minor effects, but water uptake rate is quite higher than that of original peat (1,3 %v/v/min). Water uptake rate is not only affected by clay mineralogy where clays rich in illite and kaolinite show quite stronger effects than bentonites, but also by parameters such as particle size, content of secondary oxides and sorption capacity for dissolved organic matter.

Future work focuses on the stability of peat and clay aggregation during a vegetation period, which is determined at present in tests on flocculation considering electrolyte effects of fertilizers.

Spectral properties of Rhodamine 6G in smectite dispersions: effect of the monovalent cations

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Montmorillonite monoionic forms with alkali metal and NH_4^+-cations were prepared by ion exchange. The hydration properties and binding of the ions to montmorillonite surface and the swelling properties of the mineral specimens were analyzed. Whereas Na^+- and Li^+-ions were fully hydrated over a large range of conditions, large size K^+, NH_4^+, and mainly Rb^+ and Cs^+ ions were apt to bind directly to the oxygen atoms on the mineral surface. The forms with large ions exhibited reduced hydration and swelling and the absence of macroscopic swelling of the respective aqueous colloids. The interaction of laser dye rhodamine 6G (R6G) in montmorillonite colloids was investigated by absorption and steady-state fluorescence spectroscopies. Significant effects of the properties of both the inorganic ions and swelling properties of colloidal dispersions on R6G molecular aggregation were observed. Large amounts of the molecular aggregates were formed in the colloids of Na^+- and Li^+-montmorillonites. The aggregates absorbed light at significantly lower wavelengths (~460 nm) with respect to the light absorption by non-aggregated dye (535 nm). Fluorescence spectroscopy provided a key evidence for the assignement of the type of the aggregates: The emission of the aggregates at relatively low energies proved these assemblies are rather a mixed *H*-/*J*-type than ideal *H*-aggregates. The presence of parent inorganic cations of larger size led to a significant lowering of the amount of the R6G aggregates in favor of the monomers. Investigations of the evolution of the dye aggregation with time indicated basic features of dye aggregation reaction: The size of parent inorganic ions did not affect the reaction mechanism, but rather limited the extent of the reaction. Probably the forms with large inorganic ions, such as Rb^+ and Cs^+, did not provide sufficient surface for the formation of the large size assemblies of the dye. This property can be explained in terms of strong association of the large alkali metal ions to clay mineral surface, as well as to reduced swelling in the colloidal systems of respective forms.

Characterization of Turkish kaolinite and its electrokinetic behavior in some aqueous solutions

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The interaction of kaolinite [$Al_2Si_2O_5(OH)_4$] particles is of particular importance in widespread applications, e.g., in ceramics, in the manufacture of paper (as a coating, pigment, and filler), in inks and paints (as an extender), and as an additive in the production of rubber and polymers [1]. The behavior of kaolinite particles in suspensions, pastes, and composite materials is controlled by surface chemistry properties. Investigation of the electrokinetic behavior, characterization of the particle sizes, shapes and surface properties of the particles that compose the clay is essential [2].

In the first part of study, to determine some characterization of kaolinite sample obtained from Eskişehir (Mihalıçcık) region various analysis techniques such as X-Ray Diffraction (XRD), X-Ray Flouresence (XRF), Fourier Transform Infrared- (FT-IR), Scanning Electron Microscope (SEM), specific surface area (BET), Thermal Analysis (DTA-TG), PSD (Particle Size Distribution) have been used. In the second part of the study, zeta potential (ZP) of the powdered kaolinite was investigated behavior in the presence of chloride-based metal salts (NaCl, $CaCl_2$ and $AlCl_3$) at a constant pH and also at different pHs, without metal salts.

Based on the result of semi-quantitative XRD analyses by Moore and Reynold's method [3], content of Ahirozu kaolinite is 92.2% kaolinite and 4.7% quartz and 1.1% calcite.

Investigating the variation of zeta potential of kaolinite, according to pH, it was found that it has point of zero charge (pzc) on about pH 3.5 and its zeta potential is negative above the pzc and positive under the pzc. Because of its pzc' value on about pH 2 and increasing the concentration of H^+ ions through the aqueous medium, electrical double layer is pressed and then the value of zeta potential increases to 3 mV.

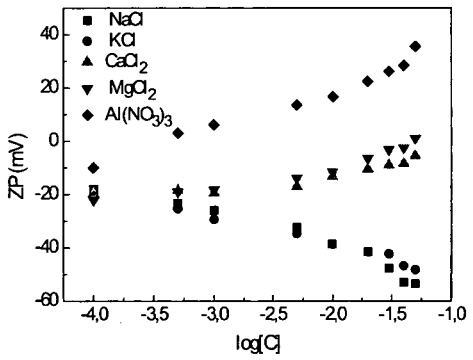

Fig. 1: Effect of the metal salts on the zeta potential of Turkish kaolinite.

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Complexation and interfacial behavior of possible environmental contaminants

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The removal of damaging chemicals has been a fundamental point in environmental research and technology, and in many related fields. For this reason, increasing attention has recently been directed to studies concerning the interfacial properties of possible environmental contaminants since they may underlie efficient technologies in treatments of soils and/or surface waters. supramolecular substances offer potential in controlling interfacial processes and represent unique models for the study of their non-covalent interactions with several chemicals.

In this paper, the relevance of inclusion complexation in improving the aqueous solubility of possible soil and water contaminants and also, the interfacial behavior of the formed supramolecular complexes are outlined. To this end, solubilization of a sparingly soluble polycyclic aromatic hydrocarbon (phenantrene, which may accumulate in soils) and a better soluble drug (carbamazepine, which may contaminate surface and ground waters) with native cyclodextrins (α-, β- and γ-cd), and with randomly methylated β-cd (rameb) or hydroxy-propyl β-cd (hpbcd), respectively, was studied in aqueous solutions. In addition, the surface properties of these chemicals and inclusion complexes at air/solution interfaces, and their adsorption from aqueous suspensions onto particles of a fractionated clay mineral (activated bentonite, particle size < 1 μm) were investigated.

The aqueous solubility of both the phenantrene and the carbamazepine could be considerably increased in solutions of suitable cyclodextrins. RAMEB and HPBCD proved to be the most efficient solubilizers for these substances. These results suggest that dissolved cyclodextrins may form inclusion complexes with each chemical. Association constants ($K_{1:1}$) for the complexes of 1:1 molar ratio have been; therefore, calculated from the experimentally determined solubility isotherms.

Certain supramolecular complexes exhibited surface activity. The complexes of both chemicals formed with the RAMEB of individually amphiphilic character and also, with the HPBCD resulted in definite reduction in the surface tension of their aqueous media.

In individual adsorption from aqueous media only slight amounts of each chemical accumulated on the Na-bentonite particles. However, the dissolved inclusion complexes adsorbed much better onto this mineral than either the individual host or the quest molecules. Especially, the carbamazepine-RAMEB and the carbamazepine-HPBCD complexes exhibited high affinity for the particle surfaces. Correlation was found between the extent of adsorption of the different inclusion complexes and their surface activity.

Preparation of modified sorbents from rehydrated clay materials

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The use of clay materials as selective sorbents of different contaminants belongs to very efficient methods [1]. A natural kaolin was calcined to metakaolin and than rehydrated at different temperatures to a highly porous sorbent. The kinetics of this process was measured, with subsequent XRD and IR characterization of arised phases [2]. The specific surface and pore distribution of new phases were also assigned. In addition, the obtained kaolin was also pre-treated with Fe^{3+} ions to improve its sorption affinity to anionic particles. Fe-modified kaolin was then used for the adsorption of As/Se oxyanions, and the adsorption efficiency in dependence on the physical chemical properties (pH, As/Se concentration) of initial solution and the surface properties of sorbent (specific surface, modification method) were investigated. The adsorption properties of newly prepared sorbents were finally compared with calcined kaolins in both raw and modified forms. The theoretical and maximum adsorption capacities of rehydrated kaolins are summarized in Table 1.

Table 1: As(V)/Se(IV) adsorption on raw and Fe-modified rehydrated kaolin under the various rehydration time

Sorbent	S(BET) (m2/g)	As(V) sorption		
		$Q_{theor.}$ (mg/g)	q(max) (mg/g)	ε(max) (%)
1 day	31,75	0,49	0,35	0,5
4 days	98,57	**0,98**	**0,65**	**5,9**
7 days	103,1	0,04	0,27	1,1
1 day-Fe	27,06	6,12	6,43	96,2
4 days-Fe	**40,66**	**6,93**	**7,33**	**96,8**
7 days-Fe	38,71	6,30	6,45	96,8

Sorbent	Se(IV) sorption		
	$Q_{theor.}$ (mg/g)	q(max) (mg/g)	ε(max) (%)
1 day	1,92	1,36	8,5
4 days			
7 days			
1 day-Fe	-	5,64	59,4
4 days-Fe	-	**7,52**	**70,7**
7 days-Fe	-	6,36	62,1

As(V) adsorption on Fe-modified kaolin ran almost quantitatively by high sorption capacities, and the procedure according to Langmuir model should be considered. Se(IV) adsorption proved a different mechanism and lower sorption capacity probably resulted from the surface and binding properties of adsorbed anion. The 4-days rehydrated kaolin demonstrated the highest specific surface and the best adsorption properties for both As(V) and Se(IV) oxyanions.

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Quantification of particle retention at natural rough black slate surfaces

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Adsorption of colloids at rock surfaces is an important environmental process. Quantitative predictions about immobilization of colloids are critical for colloid-aided contaminant transport. In the field of acid mine drainage (AMD) the retention of colloids is of particular interest because of their high potential to sorb and transport heavy metals, trace elements or radionuclides, often released during oxidative and acid rock weathering conditions [1]. Our recent studies showed that under unfavourable electrostatic conditions, the importance of surface roughness for deposition of colloids is increased [2].

Here we present a quantitative and experimental approach to investigate the relationship between micrometer to submicrometer roughness of black slates and the retention of polystyrene latex particles. Rock surface topography as well as particle retention were quantified using three-dimensional data, collected by vertical scanning interferometry (VSI). Roughness parameters (root mean square roughness, *Rq* and interfacial area ratio, *F*) were calculated based on previous studies about roughness quantification at irregular surfaces [3]. The adsorption experiments were performed as flow-through (fluid cell) and dipping experiments at pH = 6.5, where the rock surface is negatively charged according to streaming potential measurements. In a first experimental approach we used spherical particles with a diameter of 2 µm. They were negatively charged to assure conditions of electrostatic repulsion.

First results showed that micrometer-sized slopes at edges of clay mineral or organic matter aggregates are the preferred sites of adsorption of black slates (Fig. 1). Typical *Rq* and *F* values for these inclined planes of high particle density were around 0.3 µm respectively 2.8.

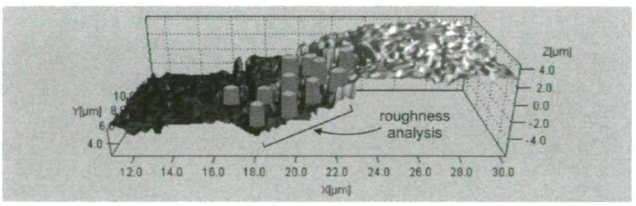

Fig. 1: High density of adsorbed particles (cylinders) at micrometer-sized slope.

Further experiments will be accomplished with smaller polystyrene particles of colloidal size. Additionally, iron and phosphate colloids will be used to resemble more AMD conditions.

[1] Fischer, C. et al. (2008) *Langmuir*, **24(7)**, 3250-3266. [2] Darbha, G.K. et al. (2010) *Langmuir*, **26(7)**, 4743-4752. [3] Fischer, C. & Lüttge, A. (2007) *Am. J. Sci.*, **307(7)**, 955-973.

Layer charge characterization of acid treated clay minerals by their interaction with methylene blue cations

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Changes in layer charge of various clay minerals upon acid treatment were studied using their interactions with methylene blue (MB) cations. This fast method is frequently used for qualitative estimation of the layer charge of smectites; however, its utilization for other clay minerals is rare. Less than 2 μm fractions of bentonites SAz-1 (Cheto, Az, USA), SWy-2 (Wy, USA) and JP (Jelšový Potok, Slovakia) containing dominantly montmorillonite were studied together with illite/smectite DVS (Dolná Ves, Slovakia), IL (Ca-illite #36, Morris, Il, USA) and kaolinite GF (Gold Field, Pugu Hills, Tanzania). Dissolution in HCl was performed at 95°C for periods of 1–36 hours.

Dye cation agglomeration at the mineral surface depends on layer charge density and results in creation of different forms of MB absorbing visible light at different wavelengths. The spectrum of MB adsorbed on SAz-1 shows a single band at 568 nm attributed to H-aggregates which are preferentially formed on the high charge surface. Two bands of similar intensities at 568 nm and 668 nm assigned to H-aggregates and monomers, respectively, prove medium layer charge density in JP. Mainly monomers absorbing at 668 nm are detected on SWy-2 confirming the lowest charge of this montmorillonite. Absorption bands of both H-aggregates and monomers appear in the spectra with DVS and IL. The intensities of the 568 and 667 nm bands indicate medium layer charge density for IL and slightly higher for DVS. The spectrum of MB on GF kaolinite shows only a band at 667 nm attributed to the monomers and proving very low charge of this sample.

The extent of structural modification of clay minerals upon acid treatment depends on the mineral type and its chemical composition. Chemical analyses of the liquid reaction products show that the dissolution rate of the montmorillonites decreases in order SAz-1>JP>SWy-2. Non-expandable interlayers in DVS and IL increase their stability in HCl as compared to montmorillonites. Kaolinite with none or minor substitution in the layers dissolves most slowly. The spectra of MB on the acid-treated samples show that the degradation of the mineral structure is closely connected with the layer charge reduction. The negative charge sites in these materials are too far each other and MB cations cannot form H-aggregates with neighbouring cations. Therefore the intensity of the H-aggregates band at 570 nm gradually decreases in favour of monomers.

The fastest decrease of the layer charge occurs for high charged montmorillonite SAz-1. The intense band of monomers at 668 nm in the MB spectrum of SAz-1 treated for 8 h confirms that the reaction product is a material of low charge density. To get similar MB spectra for middle charged JP and low charged SWy-2, at least 18 and 24 hours dissolution time, respectively, is needed. The presence of some expandable interlayers in DVS and IL allows the interaction of MB not only on the surfaces but also in the interlayer space of these minerals. The intensities of the H-aggregates and monomers bands show only small effect of HCl on the layer charge of DVS and IL upon treatments up to 12 h. On the other hand, the changes of the spectral properties are significant after 36 h, while the charge on kaolinite has not changed. The layer charge density controls the extent of MB agglomeration on natural and acid-treated clay minerals.

Thermal behaviour of ground and unground leached vermiculite

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The preparation of porous materials from clay minerals including vermiculite by selective leaching with acid has been study by several authors. The presence of iron in vermiculite plays an important role in the specific surface area obtained after acid treatment. Grinding of clay minerals significantly influences their leaching behaviour [1,2].

Ground and unground vermiculite from Santa Olalla (Huelva, Spain) was used as starting material. Vermiculite samples (<80 μm) left untreated and ground for three minutes were leached with HCl solution 1.0 M at a solid/acid mass ratio of 1:20. The suspensions were maintained at 80 °C and stirred for 24 h.

The ground vermiculite from Santa Olalla treated with 1M HCl produced a residue constituted by silica and iron oxides.The porosity studies showed that the high surface area of this residue may be attributed to the presence of iron coming from structural iron. Using HRTEM it was found that the HCl treated ground vermiculite sample consists of amorphous silica and β-FeOOH (akaganeite) microcrystals containing a small amount of Ti and Cl^- as impurities.

The DTA-TG study showed an endothermic effect at 70°C attributed to water mass loss and a small exothermic at 280°C.The XRD diagrams of the residue heated in a high temperature chamber from 30 to 1200°C at 10° min^{-1} were registered every 50°C. The starting ground 1 M HCl leached vermiculite was partially crystalline on account of presence of the crystalline β-FeOOH. This phase is present untill150 °C. Whereas the sample heated between 150 and 800°C was practically amorphous. This is in agreement with the observations that β-FeOOH decomposes to amorphous or poorly crystalline phase β-Fe_2O_3 transforming only slowly to crystalline α-Fe_2O_3. At 850 °C the sample showed the first signs of crystallinity fully developed at 1050 °C. At this temperature the sample was crystalline, consisting of quartz, cristobalite, α-Fe_2O_3 and ε-Fe_2O_3. The shifting of the crystallization temperature toward higher temperature and the consequent stabilization of the amorphous Fe_2O_3 nanophase is attributed to what is called the preventive role of the silica matrix. This effect results in fact that well crystalline iron oxide nanoparticles embedded into the silica matrix are formed usually at relative high temperatures in range 600-1000 °C in contrast to silica free material.

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[2] Maqueda, C. et al. (2009) *Appl. Clay Sci.*, **44**, 178-184.

Influence of thermal pre-treatment conditions on the reactivity of kaolinite and illite/smectite clays in alkaline and alkaline earth solutions

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Metakaolins, or alumosiliceous fly ashes are commonly used as starting materials for the generation of geopolymeric binders. Geopolymers are made by the means of reactive materials containing a certain amount of silicate and aluminate phases which can be dissolved by an alkaline medium. As a result of this, stable polymeric networks of alumosilicates will be formed [1]. The search for alternative low cost or high available resources as geopolymer raw materials is a matter of economic interest. This study focuses on the potential of kaolinite and illite/smectite clays in this regard.

The influence of the thermal pre-treatment conditions on the reactivity of the clays in alkaline and alkaline earth solutions has been investigated. Kaolinite and illite/smectite based clays were thermally activated between 550 and 950°C in oxidizing and reducing atmosphere, respectively. Changes were characterized by different methods (thermal analysis, XRD, dissolution tests). Isothermal calorimetric measurements were carried out to characterize the reaction process in alkaline media. The reached activity was followed by the degree of dehydroxylation and the amorphous content.

The potential of a raw material for the geopolymer reaction by alkaline activation can be derived from the molar ratio of soluble Si/Al in alkaline solutions. Therefore, dissolution tests in 10% NaOH solution (150 mg solid, 150 ml solution, 60°C) were carried out. Time of dissolution was varied (1d, 3d, 7d). Additionally, the standard Chapelle test was executed to determine the pozzolanic reactivity.

More Si than Al is dissolved from all samples after any dissolution time. That was already found for raw kaoline [4]. But on the one hand, the molar ratio of soluble Si/Al decreases with increasing dissolution time. On the other hand, this ratio increases with increasing pre-treatment temperature. This behaviour was remarkably influenced by the atmosphere of the thermal pre-treatment. The reactivity of the clays calcined in reducing atmosphere was higher than those calcined in oxidizing atmosphere at the same temperature.

It could be found that the influence of the thermal pre-treatment conditions on the reactivity of clays becomes more dominant in case of illite/smectite clay. The presence of 2:1 clay minerals results in a Si/Al ratio higher than 2. The dissolution of these minerals is slower than the dissolution of metakaolin. That was also demonstrated in former studies [3]. In addition to the type of clay minerals, the miner components (like calcite and dolomite) affect the molar ratio of soluble Si/Al [2].

Special attention should be paid to the determination of the optimal pre-treatment conditions when illite/smectite based clays are utilized as geopolymer raw materials.

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Computational simulations of interactions of aflatoxin B1 with smectite

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Adsorption isotherms, animal feed and human diet trials have demonstrated the effectiveness of smectite-rich bentonites in reducing or alleviating the toxicity of aflatoxin B1 (AfB1). More and more spectroscopic and mineralogy data have been accumulated to elucidate the molecular mechanisms of reactions between the mycotoxin and the minerals. Unambiguous explanations, however, have been hindered by the complexity of the spectra and lack of definite assignments on the vibrational bands. The objective of this study was to verify and refine the theories about the bonding of AfB1 to smectite. We conducted computational simulations to find the theoretical band positions in the hypothesized models and compared the simulated patterns with the experimental data to find the best match. Geometry optimization and theoretical IR spectra for aflatoxin and aflatoxin-smectite complexes were performed with density functional theory (DFT) at PCM/B3LYP/DGDZVP level of theory.

It was found that in the humid environment AfB1 forms complexes with smectite through water bridges between AfB1 and exchange ions in smectite. On the other hand, at 0% humidity AfB1 carbonyl groups were connected to the ions through ion-dipole interactions. The experimental spectra were in excellent agreement with theoretical calculations. The calculation allowed accurate assignments of the bands of experimental spectra.

Organoclay-herbicide interaction mechanism as affecting the bioavailability of organoclay-based formulations of atrazine in soil

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Organoclays have been proposed as pesticide supports to prolong the efficacy and reduce the large runoff and leaching losses that usually suffer pesticides when they are applied in an immediately available form [1]. The bioavailability of several organoclay-based formulations of atrazine for bacterial degradation in soil was studied. Two different organic cations, L-carnitine (CAR) and hexadecyltrimethylammonium (HDTMA), were incorporated into Na-rich Wyoming montmorillonite (SW) and Ca-rich Arizona montmorillonite (SA) as a strategy to enhance the affinity of the clay minerals for atrazine (Table 1), and then organoclay-based formulations of atrazine were prepared by supporting the herbicide on the organoclays.

Table 1: Some characteristic of the organoclays used

Organoclay	OCTS[1]	d_{001} (Å)[2]
SW-CAR	61	14
SW-HDTMA	100	18
SA-HDTMA	101	24

[1]Percentage of the CEC of the clay compensated by organic cations, [2] Basal spacing value (Å)

Solvent extraction methods were used to correlate atrazine residue bioavailability in soil to atrazine mineralization using an atrazine degrading bacterium. A soil from Minnesota (USA) was treated with the organoclay-based formulations of ^{14}C-atrazine and with free ^{14}C-atrazine, and then inoculated with *Pseudomona* sp. strain ADP, a microorganism capable of rapidly mineralizing atrazine. Evolved-$^{14}CO_2$ was determined during a two-week incubation period. The amounts of ^{14}C-atrazine residues distributed between the aqueous-extractable, metanol-extractable, and bound fractions in the soil were determined at t=0 and after the two-week mineralization period, for the different formulations assayed.

Results indicated that non-extractable atrazine residues in soil increased with aging and that the mineralization rate of atrazine adsorbed on SW-HDTMA and SA-HDTMA decreased with the affinity of the organoclay for the herbicide. However, the formulation based on SW-CAR displayed a distinct behavior. Despite the very high affinity of SW-CAR for atrazine, mineralization occurred at a similar rate compared to that found for the free herbicide. Desorption experiments demonstrated that atrazine is readily released from SW-CAR at high pH levels, such as that provided by the soil tested, making the herbicide immediately available for degradation.

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Improving the wettability of peat based growing media by the amendment of clay

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Clays are widely used in horticulture for the amelioration of the chemical and physical properties of peat based growing media. A common problem of such substrates rich in organic matter arises from their poor wettability in the dry state. Up to now, less is known on how clay amendments differing in mineralogical composition and other mineral parameters affect the wettability behaviour of peat based growing media. In this study special emphasis was given on the adsorption of peat derived dissolved organic matter (DOM) onto the external surfaces of clay minerals in the substrate, as this process may render a clay surface from hydrophilic to hydrophobic.

Seven different clays varying in their mineral parameters (texture, mineralogical composition, cation exchange capacity (CEC), specific surface area (SSA) and oxalate and dithionite soluble Fe and Al) were used to investigate their effect on wettability and water uptake characteristics on a peat blend with a moderate degree of decomposition. The wettability was assessed in terms of contact angle (CA) measurements, calculation of surface free energies (SFE), and water uptake measurements using a capillary rise method (CRM). Differences in the affinity for peat derived DOM was determined in batch adsorption experiments and variations in the kind of adsorbed DOM fractions were traced by UV-Vis spectrometry before and after adsorption.

The wettability of peat based growing media was markedly influenced by the amount and kind of amended clay. Both, the substrate wettability as well as sorption of peat derived DOM onto clay surfaces showed strong relation to mineral parameters. Sorption of DOM increased with increasing CEC, SSA, Fe_d, and $\sum Fe_o+Al_o$ of the clays, while the substrate wettability was negatively correlated with the SSA ($r^2 = 0.66$), CEC ($r^2 = 0.69$), Fe_d ($r^2 = 0.68$) and $\sum Fe_o+Al_o$ ($r^2 = 0.61$). By considering the amount and kind of mineral bound DOM species, a non-linear regression explained 69% and 85% of the variations in substrate wettability. Overall, the results provide a useful basis for the selection of suitable clay amendments for improving the wettability of peat based growing media.

Nanocomposite clay minerals with fluorescence properties based on intercalation of kaolinite

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The topic of this contribution is preparation of new organomineral derivatives, because they combine the structural, physical and chemical properties of both the inorganic host material and the organic guest species at a nanometer scale [1]. Kaolinite, despite its wide abundance in nature [2] and interesting intercalation properties [1,3] has been less studied as a precursor mineral for new organomineral materials, when compared to the smectite clays for example [4], presumably due to the difficulty in expanding the interlayers of kaolinite compared to other expandable layered materials. Methods based on the modification of preexisting inorganic structures offer considerable flexibility in the design of new hybrid materials [5].

This study has shown that the new inorganic - organic layered hybrid materials with fluorescent properties based on kaolinite can be prepared by intercalation of laser dye Coumarine 4 using guest – displacement reaction with ethylene glycol according to [6]. Prepared material was characterized using X - ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

New type of inorganic – organic nanocomposite based on intercalation of kaolinite with fluorescent dye could be used to prepare antiseptic systems (e.g. painting colours, textile fibres etc.) because these systems have potential to produce singlet oxygen which has antiseptic and disinfecting effects.

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Thermal treatment of organoclays enhances their sorptive potential: a weakened water-organic sorbate competition on mildly heated sorbents?

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Recently, we have observed that thermal treatment of organoclays (formed by exchange reactions between organic cations and inorganic cations of a clay mineral) can improve their ability to sorb organic compounds from water [1,2].The aim of the presented work is to examine how this thermal treatment effect is related to the structure of organic sorbates and exchanged organic cations. The organoclay sorbents were prepared from Wyoming bentonite through replacing exchangeable Na+ by n-hexadecyltrimethylammonium (HDTMA), tetraethylammonium (TEA) and benzyltrimethylammonium (BTMA). Then, the organoclays (and Na-bentonite itself) were heated at 150, 250, 360 and 420oC for 2 hours in air and subjected to aqueous sorption of a series of probe organic compounds (phenanthrene, nitrobenzene, atrazine, phenol, m-nitrophenol) capable of different types of molecular interactions. We have demonstrated that a mild heating (at 150 0C) of organoclays can result in a distinct increase of a sorptive efficacy of sorbents. As follows from XRD, FTIR, elemental composition and TG data, this mild thermal treatment of organoclays is associated with fairly small changes (if any) in the sorbent structure.

Heating of organoclays at higher temperatures results in a loss of organic carbon and significant changes in the organoclay structure. Further improvement of a sorptive efficacy as compared with treatment at 150 0C, if occurs, is minor. This was in contrast to our earlier expectations of a significant contribution of charcoal and oxidized organic matter formed in the clay interlayer space to the organic sorbates-organoclay interactions. It is suggested that a mild thermal treatment of clay-based sorbents results in a partial loss of a sorbent ability to rehydrate in aqueous solutions thus weakening water-sorbate competition for sorption sites on a mildly heated sorbent, and therefore, increasing a potential of organoclays to sorb organic compounds from water. In particular, organic sorbates capable of specific interactions with siloxane surfaces may demonstrate the increase of sorption on a pre-heated organoclay. In organoclays with long-chain organic cations (e.g. HDTMA) capable of additional blocking the clay surface, the enhancing effect of thermal pre-treatment on sorption of organic compounds may be mitigated as compared with organoclays formed by smaller-size organic cations (e.g. TEA and BTMA).

A parallel is hypothesized between a mechanism suppressing a hydration of a sorbent after its mild thermal pre-treatment and a recognized fixation of certain inorganic cations occurring during clay heating at higher temperatures. Important implications associated with the observed phenomena include a possibility of activating organoclays for environmental applications and a better understanding of relative role of natural organic and clay components in retention of organic pollutants by environmentally important sorbents influenced by elevated temperatures (e.g. soils affected by fire).

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Simultaneous sorption of lead and phenol by bentonite and organobentonite

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Clays or organoclays have been used as barrier to prevent the transport of hazardous contaminants in landfills. However, clays are known to effectively sorb mostly inorganic contaminants, while organoclays are mainly used for organic contaminants. Since the organoclays are basically clay particles modified with cationic surfactants, there might be an optimal coverage of cationic surfactant on the clay particles to sorb both inorganic and organic contaminants. In order to determine the optimal mass of cationic surfactants on the bentonite, bentonites were treated with various ratios of dodecyltrimethylammonium bromide (DDTMA) and benzyldodecyldimethylammonium bromide (BDDDMA). The role of the benzyl group of surfactant molecules was also studied in the sorption processes.

Phenol and lead were selected as representative contaminants. Sorption kinetics and isotherms of contaminants by both organobentonites were selectively studied in the function of surface coverage. When either phenol or lead exists as a single contaminant, phenol sorption increased with increasing DDTMA and BDDDMA to bentonite ratios, and lead sorption decreased with increasing DDTMA and BDDDMA to bentonite ratios. Sorption of phenol was a function of DDTMA and BDDDMA coverage on the bentonites, while lead sorption was much more influenced by the initial lead concentration than the mass of surfactants added to the bentonites.

Hydrotalcite – like compounds as adsorbents of phenols and their environmental applications

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This work is devoted to studies of processes of sorption of phenols by synthetic clay minerals of different composition.

To prevent dangerous contamination of the environment, industrial wastewaters should be cleaned from pollutants such as phenols [1]. The problem of pollution of natural waters, the growth in the amounts of waste waters and the search for effective methods of cleaning them are realy urgent.

The purpose of this work is the search for new anionic sorbents. Their application would help to effectively remove phenols from wastewaters.

The most promising sorbents are those based on double hydroxides of metals with the structure of hydrotalcite. They are cheap, accessible and effective, universal sorbents, with a high absorption capacity, resistance to environmental stress and can serve as excellent carriers for fixing on the surface various compounds including their modification.

The 2:1 clay minerals capable of changing the interlayer distances are very effective. Water molecules, as well as the cations and anions can be adsorbed also in the interlayer space of these minerals. Therefore it is possible to place large ions between the layers and form columns to create a system of pores where various small molecules can be placed. The pores size resulting in the intercalation process is about several tenths of nanometers. The samples were synthesized with the following ratios of cations in the matrix (Table 1).

Table 1: Samples of LDHs

MgO, mol/mol	k, мol/l·s
0,52	833,3
0,72	1290,3
0,81	1666,7
0,86	1739,1

The specific surface of LDHs was determined by low-temperature nitrogen adsorption chromatographic method with subsequent processing of the results obtained by BET method.

The change of interlayer distance in LDHs after the adsorption of phenol, were investigated.

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Nanotubular particles derived from kaolin group minerals - structural and textural examination

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Modified intercalation/deintercalation method was used to increase the efficiency of nanotubes formation from kaolin group minerals differing in degree of structural order [1]. At variance with our earlier work [2], methanol was used instead of 1,3-butanediol for the grafting reactions. The intercalation of hexylamine was followed by intercalation of octadecylamine [3]. Materials obtained by different procedures were subjected to detailed physico-chemical characterization (nitrogen adsorption/desorption, XRD, FTIR, DSC and TEM). The use of methanol instead of 1,3-butanediol led to a significantly different result. The content of nanotubes was much higher in the case of "Maria III" kaolinite samples containing minerals of high structural order. Poorly ordered samples ("Jaroszów kaolinite and "Dunino" halloysite) yielded less nanotubes than in the case of grafting with 1,3-butanediol. Enhanced formation of nanotubes in "Maria III" kaolinite was tentatively attributed to higher reactivity of well ordered kaolin minerals toward methanol rather than 1,3-butanediol, resulting in a more efficient amine intercalation. The additional intercalation of longer chain octadecylamine significantly increased the content of formed tubes.

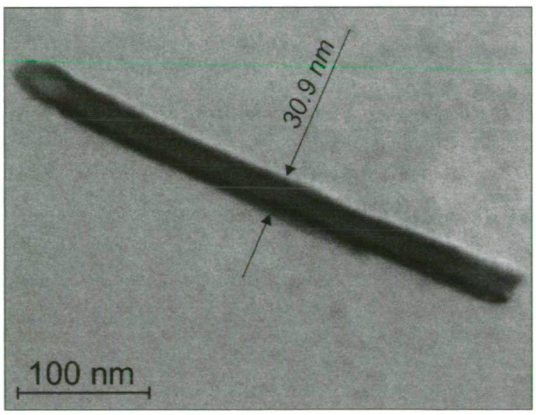

Fig. 1: TEM microphotograph of a kaolinite nanotube.

The diameters of rolled layers observed by TEM were ca. 30 nm (Fig. 1) and corresponded to diameters of newly formed group of pores detected by textural analysis. This confirmed that nanotubes contributed to a significant increase of surface area and total pore volume, observed for "Maria III" kaolinite. In the case of "Jaroszów" kaolinite and "Dunino" halloysite the changes of textural parameters were connected with the presence of macropores and mesopores with diameters different from these observed for nanotubes. These pores were assigned to interparticle and interaggregate spaces in stacks of platey particles and small amount of nanotubes.

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Halloysite–TiO_2 and palygorskite–TiO_2 nanocomposites: synthesis and photocatalytic activity in decomposing air pollutants

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In the present study TiO_2/clay nanocomposites were sythesized by dispersion of TiO_2 on the surfaces of two different natural clay minerals, palygorskite and halloysite, in order to increase the dispersion of TiO_2 and therefore its photocatalytic action. Deposition of TiO_2 on the clay minerals surfaces were conducted by using a sol-gel method with titatnium isopropoxide as a precursor under hydrothermal treatment at 180 °C. The phase composition, particle morphology and physical properties of the samples were characterized by several analytical techniques including XRD, SEM-EDS, TEM, ICP, ATR-FTIR, BET and porosimetry analysis. The synthetic procedure allows the homogeneous distribution of TiO_2 grains on the surfaces of the clay minerals leading to the improvement of the properties and potential uses of the nanocomposites. It was found that after treating with TiO_2, the halloysite and palygorskite samples showed mesopores of about 5.6 and 6.5 nm, respectively, while the macropores of halloysite (lumen) disappeared. The latter is attributed to the covering of the lumen of halloysite tubes by TiO_2 nanoparticles and for that reason the pore size of the TiO_2–treated halloysite was significantly smaller. The photocatalytic efficiency of clay-titania nanocomposites was measured in decomposing NOx, CO_2, and CH_3CHO gas. The supported catalysts showed higher activity in decomposing NO*x* gas and lower in CO_2 and CH_3CHO gas under visible-light irradiation (λ> 510 nm) and UV light irradiation (λ> 290 nm) compared to that of the standard commercial titania, P 25.

Effect of oligomerically modified montmorillonite on morphologies and properties of polycarbonate/montmorillonite nanocomposites

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Great efforts have been paid to polymer-clay nanocomposites in the past decades since those materials possess significantly improved physical [1] and other properties including thermal stability [2] and decreased flammability [3,4] over the virgin polymer.

In this work, two oligomeric surfactants (COPS-B and COPS-O) as shown in Fig. 1 were used to treat sodium montmorillonite via standard ion-exchange methods to give thermally stable oligomerically modified montmorillonites to prepare polycarbonate/montmorillonite nanocomposites (PC/MMT) by melt processing using a twin screw extruder.

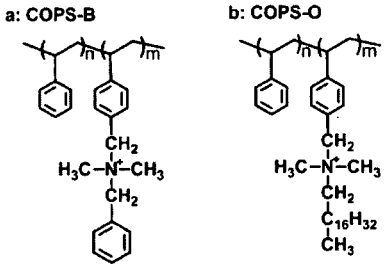

Fig. 1: Structure of oligomeric surfactants used to treat sodium montmorillonite.

The results of TEM and XRD indicated that the PC/MMT nanocomposites had partially exfoliated and partially intercalated structures. Both clay loading and organic treatment structure of MMT influenced the morphologies and properties of the nanocomposites. The structure similarity, i.e., the strong interaction, between the polymer matrix and the organic treatments of the clay was a critical factor for controlling clay dispersion and exfoliation, and hence the mechanical and the heat insulation properties of the nanocomposites.

Analysis of all the composites indicated that once the clay mineral loading exceeded a critical value, it became a negative factor for forming high level dispersion to obtain better mechanical properties. Good mechanical properties of PC/MMT nanocomposites were obtained with a clay loading less than 2 wt%. A thermal-stable organic treatment was crucially important for an expected nanocomposite system with good thermal stability. It partly depended on the organic treatments of MMT used in the composites.

Great differences were observed between COPS-B and COPS-O composites. COPS-B showed visible advantage to COPS-O. Benzyl group of COPS-B in composites might play an important role in the process.

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Bentazone and phenanthrene adsorption on external montmorillonite surface - Monte Carlo modelling

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Bentazone and phenanthrene are pesticides with different fate in soil. Bentazone can be rapidly transported by infiltrating water into ground water due to its high solubility, minimal sorption to soil particles, and low degradability. On the contrary, phenanthrene is retained by sediments and soil materials. The mechanism of the retention of nonionic hydrophobic organic compounds in soil is still debated and has been attributed to their partitioning either to organic matter or to soil clay minerals. A recent study has reported on strong phenanthrene sorption capacities of smectites, which are comparable to those of soil clays containing a considerable amount of organic matter [1].

In order to address open questions, the structural and energetic characteristics of bentazone and phenanthrene interaction with external surface of montmorillonite were studied using Monte Carlo simulations at ambient conditions. In the first part of this work, the adsorption of the studied molecules at the montmorillonite-air and montmorillonite-water interface is simulated in a constant *NVT* ensemble using the Metropolis algorithm for sampling structural properties. The simulations predict the most favourable alignments of adsorbed molecules in dependence on the varying coverage and on the thickness of the adsorbed water film. In the second part, an expanded ensemble density of states method [2] based on the Wang-Landau algorithm [3] is applied to the equilibrated systems for sampling potential of mean force profiles between the adsorbed molecule and the montmorillonite surface. Reaction path coordinate is defined as the distance between the centre of mass of the molecule and the montmorillonite surface. The following possible reaction paths are explored: (1) above a free octahedral substitution, (2) above a ditrigonal cavity centre near a tetrahedral substitution paired with Na+ ion, and (3) above a tetrahedral Si site near the octahedral substitution chosen in (1). The simulations predict the most favourable reaction path between bentazone/phenanthrene and the montmorillonite surface. A discussion on the detailed molecular-scale data on the preferred adsorption positions of the studied pesticides at the montmorillonite-water and montmorillonite-air interface based on the calculated free energy profiles will be given.

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Molecular dynamics simulation of TCDD adsorption on clay mineral

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Adsorption of organic toxicants on clay minerals is now receiving considerable attention, because contact with clays is thought to influence the transport, toxicity and bioavailability of the organic toxicants in the environment. Although experimental methods have been employed to investigate the adsorptive characteristics (e.g., batch equilibrium adsorption, spectroscopic characterization), molecular simulations represent a significant complementary approach because they can provide atomic-level insight into the adsorption process.

We report our recent research work about TCDD (2,3,7,8-Tetrachlorodibenzodioxin) adsorption on pyrophyllite and montmorillonite using molecular dynamics simulations. One of the central challenges is to develop and apply an effective force field between the pollutant and clay surfaces. We have considered a number of models. One of the most efficient is where the clay minerals were built using the ClayFF model from Cygan et al [1], and the CVFF force field was used to build TCDD and clay-TCDD potential.

Table 1 lists the adsorption energies of TCDD on the outer surface and interlayer of pyrophyllite and montmorillonite using these models within the NVT ensemble at 300K.

Table 1: Adsorption energy of TCDD on clay minerals (eV)

	Pyrophyllite	Montmorillonite
Surface	-0.44	-0.83
Interlayer	5.33	3.60
Interlayer[a]	-0.62	-1.51

The adsorption energy of TCDD on pyrophyllite was comparable with the results from DFT calculation [2], while on montmorillonite the adsorption energy was more negative. This indicates a stronger interaction between TCDD and montmorillonite. Examination of the structure shows that the interaction between K^+ and TCDD accounts for the larger adsorption energy at the montmorillonite surface.

The intercalation energies of TCDD for both pyrophyllite and montmorillonite are highly positive, because this contains the energy to separate the two layers and insert the TCDD molecule. This strong interaction between the layers of the clay minerals has also been shown by Heinz et al [3].

In another simulation, we inserted TCDD into the interlayer region but with the layers already separated. Thus, the energy for separating the layers is excluded. In this case, the adsorption energies were more negative than for the free surface (Table 1). This was because both the two layers could contribute to the adsorption of TCDD.

The above results show that although TCDD could interact strongly with clay minerals in the interlayer region, the large energy for separating the sheets could prevent the adsorption into the interlayer space of the clay minerals. However, once the layers were separated by other pillars (e.g., organic cations), the clay minerals are predicted to strongly adsorb the organic toxicants, and then influence their environmental behaviours.

Acknowledgements: This work was supported by the Royal Society-BP-Amoco Research Fellow project (RC-H1054).

[1] Cygan, R.T. et al (2004) *J. Phys. Chem. B*, **108**, 1255-1266. [2] Austen, K.F. et al (2008) *J. Phys.: Condens. Matter*, **20**, 035215. [3] Heinz, H. et al (2006) *J. Chem. Phys.*, **124**, 224713.

The influence of heteropolyacids on the textural properties of Fe-montmorillonite

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Intercalated clays present great interest as supports for synthesis of new catalysts [1]. For synthesis of composite metal-oxide materials with high disperse uniform distribution of metals it is perspective the use polyoxometallates, containing several metals atoms in the structure of their complex ions [2].

Materials have been synthesised using two methods: I - adsorption of heteropolyacids $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ on Fe-montmorillonite (Fe-MM-500°C) calcinated at 500°C; II - simultaneous introduction of pillaring solution (1M $FeCl_3$ + 1M NaOH) and a solution containing the heteropolyacids into suspension of clay previously dispersed by ultrasound (22 kHz, 3 min). The preparation Fe-MM method was described in our early work [3]. All the samples were calcinated at 500°C for two hours.

The samples obtained belong to mesoporous materials (Fig. 1), but the samples obtained by method II contain also micropores which surface area is equal to 5.0-17.7 m^2/g (Table 1). At that the treatment by heteropolyacids in both cases leads to a decrease in specific surface area and pore volume in comparison with Fe-MM, that may be caused by adsorption of polyoxometallates in their mesopores.

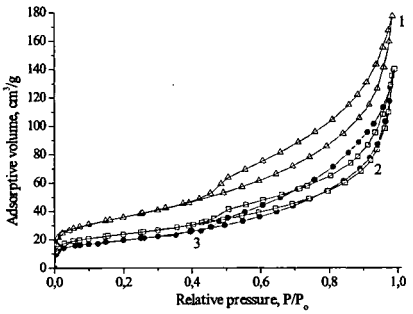

Fig. 1: N_2 adsorption/desorption of samples: 1- Fe-MM, 2- $SiMo_{12}$/Fe-MM (I) and 3- SiW_{12}/Fe-MM (I).

The Fe content in the samples is 4.0-4.6 wt.%. The quantity of introduced Mo and W depends on the method of synthesis of the material. The content of W in the samples SiW_{12}/Fe-MM obtained by method I and II is 1.82wt.% and 0.17 wt.% accordingly. The content of Mo in the samples $SiMo_{12}$/Fe-MM is 1.13wt.% (method I) and 0.53 wt.% (method II).

Table 1: Textural characteristics of composite materials

Materials (method)	Fe wt.%	W(Mo) wt.%	S_{BET} m^2/g	ΣV pore cm^3/g	D_{pore} Å	S_μ m^2/g	ΣV_μ cm^3/g
Fe-MM	4.6	0	128	0.274	85	-	-
SiW_{12}/Fe-MM (I)	4.5	1.82	84	0.217	103	-	<0.001
SiW_{12}/Fe-MM (II)	4.0	0.17	93	0.235	101	5.0	0.003
$SiMo_{12}$/Fe-MM (I)	4.4	1.13	70	0.216	123	-	<0.001
$SiMo_{12}$/Fe-MM (II)	4.6	0.53	92	0.183	80	17.7	0.009

S_{BET} – surface area, ΣV pore – total volume pore, D_{pore} – diameter pore, S_μ - surface area of micropore, ΣV_μ - volume pore of micropore.

The results of this work confirm the possibility of application of Fe-MM as supports for synthesis of catalysts.

[1] Marme, F. et al. (1998) *Micropor. Mesopor. Mat.*, **22**, 151-163. [2] Yadav, G.D. (2005) *Catal. Surv. Asia*, **9**, 117-137. [3] Shapova, M.A. et al. (2002) *Chem. Sustain. Development*, **10**, 347-353.

Dispersion influence on activation energy of kaolinite dehydratation

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Kinetics of kaolinite dehydratation has been studied for many decades revealing that, depending on the degree of structural perfection, concentration and extensive defects, the activation energy of dehydratation reaction changes within the range of 80-175 kJ/mol, significantly changing the reaction rate. According to the particle size, kaolinite belongs to so-called nanocrystalline materials, being characterized by size effects: dependence of material properties on its dispersivity. It was shown theoretically and experimentally in Piloyan & Bortnikov [1] that activation energy of reaction should decrease with dispersivity increasing. Using the approach developed in Piloyan & Bortnikov [1], in the present work the influence of dispersions on kaolinite activation energy has been investigated. As the object of study the alluvial kaolinite from Zhyravliny Log deposit (South Ural) has been chosen. The different technologically important kaolinite fractions (10-5, 5-1, 1-0.5, <0.5 μm) have been investigated by the method of transmission electron microscopy (including SAED and HRTM). Following the methodology of Piloyan & Bortnikov [1], the formula connecting the size of the coherent dispersion block with activation energy of dehydratation reaction and surface enthalpy has been received:

$$\ln(r) = A - \frac{E}{RT_m} + \frac{2H_F}{r\rho RT_m} - B\ln(I)$$

Where A and B are constants, r – the size of coherent dispersion block, E – energy of activation, R – gas constant, H_F–surface enthalpy, ρ – molar density of kaolinite, T_m – temperature of thermal effect peak on DTA curve, I – index of thermal effect form. Using experimental data the following regression equation was obtained

$$\ln(r) = 29.8887 - 21248.6 T_m^{-1} + 17.2323\, T_m^{-1} r^{-1} - 3.48522 \ln(I)$$

From this equation it has been found, that the activation energy of dehydratation reaction for kaolinite macrocrystals is 176,6 kJ/mole, that is characteristic for well crystallized kaolinites. Surface enthalpy is 0.73 J/m^2 coinciding (within the limits of experimental error) with the value of 0.62 J/m^2, obtained in Salles et al. [2]. The results obtained are shown in Table 1.

Table 1: Experimental data for the kaolinite studied

Fraction (μm)	Kaolinite content (%)	T_mK	I	r (nm)	E kJ/mole
10-5	86,4	823	1,56	27	171,3
5-1	89,3	833	1,85	23	170,4
1-5	89,24	848	2,4	17	168,2
<0,5	88,64	833	2,5	15	167,1

[1] Piloyan, G.O. & Bortnikov, N.S. (2010) *Dokl Akad Nauk*, **432**, N3. [2] Salles, F. et al. (2006) *J Colloid Interf Sc*, **303**, 617-626.

Role of clays in the preservation of organic matter

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It is commonly admitted that clay minerals can play a major role in the preservation of organic matter under aquatic environments and their transfer to sediments. The mechanisms of fixation of organic molecules by clays remain obscure. Series of *in vitro* and *in vivo* experiments have been performed, under marine and lacustrine environments, with synthetic saponites of variable charge and a natural low-charge montmorillonite.

This study shows the absence of intercalation of organic molecules in the interlayer space of clays. Only sorption on clay surfaces and edges occurs. *In vitro* experiments show that organo-clay interactions are mainly controlled by the type of organic molecules and particularly by the nature of their functional groups. *In vivo* experiments indicate that fresh organic matter is more easily adsorbed than diagenetically evolved one. The clay surface charge density also controls the nature and concentration of adsorbed organic species. Under lacustrine environments, a selective sorption of aromatic molecules is observed on low-charge clays.

Attempts to destabilize the obtained organo-clay compounds, by hard alkaline treatment, were unsuccessful and indicate the great stability of these associations, with strong and probably multiple bonds. Owing to this high stability of organo-clay assemblages, the organic matter becomes unavailable to benthic fauna and bacteria in natural environments.

Therefore, sorption on clays can be considered as one of the preservation mechanisms of organic matter and controls the incorporation of metabolisable molecules into sediments.

Ag- and Cu-vermiculite nanocomposites and their antibacterial effect

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Clay minerals belong to the important materials which can serve as metal nanoparticles matrixes thanks to their structural properties. In this study, vermiculite from Brazil was used as starting material. Beside montmorillonite [1, 2], vermiculite is sometimes used as a matrix for silver and copper nanoparticles [3].

Vermiculite (V) was treated with different molar concentrations of aqueous solutions of $AgNO_3$ and $Cu(NO_3)_2$ and Ag-V, Cu-V, Ag,Cu-V materials were synthesized. Samples were evaluated for the effect of solutions concentrations on the quantity of Ag and Cu, structure changes of vermiculite and antibacterial activity.

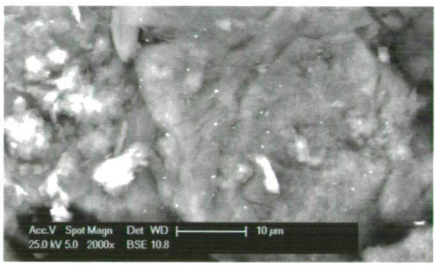

Fig. 1: The SEM micrograph of Ag-V (white dots represent Ag agglomerates on the vermiculite surface).

The morphology was studied using scanning electron microscopy (SEM). The SEM micrograph of Ag-V (Fig.1) showed agglomerates of silver nanoparticles anchored on the vermiculite substrate. Powder X-ray diffraction (XRD) was employed mainly to determine the interplanar spacings in the starting clay minerals and in the Ag- and/or Cu-V composites. The XRD patterns showed Ag (111) reflection of metallic silver. According to the basal reflection (001) intercalation of Ag and Cu into interlayer space of vermiculite was supposed.

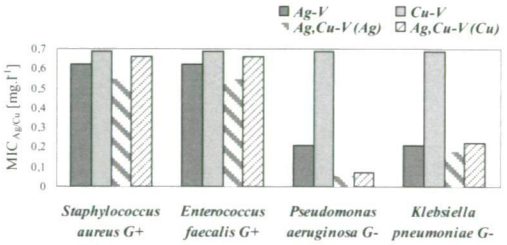

Fig. 2: The MIC Ag/Cu (Minimum Inhibitory Concentration of Ag and Cu) was determined by the lowest concentration that completely inhibits visible bacteria growth.

The antibacterial activity tests on the Gram positive (G^+) and Gram negative (G^-) bacteria strains showed dependence of antibacterial effect upon content of Ag and/or Cu with the result that the highest effect was observed against G^- bacteria (Fig. 2).

Acknowledgements: The work was supported by projects: Ministry of Education, Youth and Sport of Czech republic (SP/2010111) and Czech Grant Agency (GA ČR 205/08/0869).

[1] Valášková, M. et al. (2007) *J. Nanosci. Nanotechnol.*, **8**, 3050-3058. [2] Magaña, S. M. et al. (2008) *J. Mol. Catal. A-Chem.*, **281**, 192-199. [3] Li, B. et al. (2002) *J. Min. Mat. Char. & Eng.*, **1**, 61-68.

Preparation of oriented films of layered double hydroxides with photoactive properties

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Layered double hydroxides (LDHs) represent suitable hosts for intercalation of various anionic species. The intercalated LDHs attract increasing attention in various medical applications as drug carriers, gene therapy, etc. [1]. Photoactive molecules such as porphyrins can be excited by visible light to the triplet states that rapidly interacts with molecular oxygen by energy transfer to form singlet oxygen, $^1O_2$, a highly reactive oxidation agent with cytotoxic effects enabling its application in photodynamic therapy. In our recent reports [2,3], the structural and photophysical properties of LDH powders and oriented films with intercalated porphyrin sensitizers were described and the formation of singlet oxygen followed by its diffusion to solid-liquid or solid-gas interfaces was proven.

The oriented LDH films were prepared on quartz substrates by deposition from a colloidal suspension of delaminated LDH particles. Two colloidal suspensions were prepared. The first one was obtained by delamination of coprecipitated Mg-Al-NO_3 LDH in formamide. Second, the acetate form of Mg-Al LDH was used for the preparation of a colloidal suspension in water: nitrate anions in Mg-Al-NO_3 LDH were exchanged in an aqueous solution in an excess of sodium acetate and the washed product was dispersed in distilled water [4]. Porphyrins 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin or Pd(II)-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin were embedded in oriented LDH films prepared by the layer-by-layer technique. The absence of non-basal diffraction lines in powder XRD patterns confirmed a preferential arrangement of LDH particles parallel to the substrate surface. Transparent films were obtained, their absorbance in visible light increased gradually with the number of deposition steps (Fig. 1). The photophysical properties of the prepared LDH/porphyrin films including the formation of singlet oxygen are discussed.

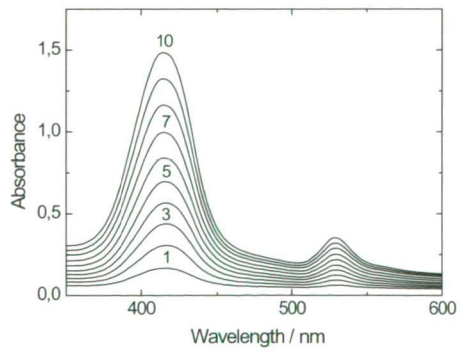

Fig. 1: Absorbance of the oriented LDH/porphyrin film increasing with the number of deposition steps (up to 10 deposition steps were applied).

Acknowledgements: This work was supported by the Czech Science Foundation (P207/10/1447) and by the Ministry of Education, Youth and Sports of the Czech Republic (MSM 6046137302).

[1] Del Hoyo, C. (2007) *Appl. Clay Sci.*, **36**, 103-121. [2] Lang, K. et al. (2007) *Chem. Mater.*, **19**, 3822-3829. [3] Lang, K. et al. (2008) *Chem. Phys. Phys. Chem.*, **10**, 4429-4434. [4] Iyi, N. et al. (2008) *Langmuir*, **24**, 5591-5598.

Potassium acetate-intercalated kaolinite obtained by mechanochemical and aqueous suspension techniques – a comparative study

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Intercalation complexes of a high-defect kaolinite have been prepared by direct reaction with potassium acetate solution as well as by co-grinding with potassium acetate in the absence of water (mechanochemical intercalation). Potassium acetate-intercalated high-defect kaolinite has been aged for up to 2 months. The aged and non-aged complexes were studied by X-ray diffraction, thermal analysis, DRIFT spectroscopy and electron microscopy. Ageing of the mechanochemically intercalated kaolinite increases the degree of intercalation [1] by almost 20 %, as well as decreases the structural deformation of the intercalation complex. At the same time, the aqueous suspension technique creates kaolinite–potassium acetate intercalation compound which shows practically no change after ageing.

[1] Wiewiora, A. & Brindley, G.W. (1969) *Proc. Int. Clay Conf.*, Tokyo, **1**, 723.

Time- and pH-dependent sorption of veterinary antimicrobial sulfamethoxazole to bentonite and organobentonite

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Sulfonamide antimicrobials comprise a class of synthetic sulfanilamide derivatives which are used in human therapy, livestock production and aquaculture. Substantial amounts of sulfonamides, ionizable, polar veterinary, may reach the environment through grazing livestock and spreading of manure on agricultural soils. Further pathway into the environment is direct use in aquaculture. Residues of sulfonamides have been found in soils and adjacent environmental compartments [1,2]. In soils, parts of added sulfonamides are retained over months [1]. Sorption to soils and sediments is a crucial but not sufficiently understood process influencing the environmental fate of sulfonamides.

The objective of this study was the influence of contact time and pH on sulfomethoxazole sorption to native bentonite (Rátkai Pettyes, Hungary) and surfactant-modified bentonite. The sulfamethoxazole (pK_a = 4.7) was analyzed by capillary electrophoresis using Tris (tris(hydroxy-methyl)aminomethane) at pH of 8.3. Organobentonites were prepared from bentonite by using benzyldodecyldimethylammonium (C_{12}) bromides. The degree of modification was 100 % (C_{12}-100-B) and 50 % (C_{12}-50-B) of the cation exchange capacity. Adsorption kinetics and isotherms determined in aqueous suspensions using batch technique were modelled.

The bentonite sorbent was expected to interact mainly with cationic sulfonamide at pH < 4.7, above this pH value little adsorbed amount could be measured (q_s = 1.5 - 2 mg/g at pH 6.4 in natural form without pH adjustment). Modification of bentonite surfaces by benzyldodecyldimethylammonium assisted the sulfamethoxazole adsorption (q_s = 4 - 5 mg/g at pH 6.4 in natural form without pH adjustment). Following the adsorption kinetics five days was needed to reach the adsorption equilibrium.

Our results imply that inorganic sorbents compared to organic substances can play a minor role for sulfonamide sorption in many soils and sediments. Especially the potential of organic sorbents for increased sorption with contact time would be important. On the other hand organobentonite (modified by benzyldodecyldimethylammonium bromide) could be used as biosorbent material in soil and sediment remediation.

[1] Thiele-Bruhn, S. et al. (2004) *J. Environ. Qual.*, **33**, 1331-1342. [2] Hamscher, G. et al. (2005) *Environ. Toxicol. Chem.*, **24**, 861-868.

Spectroscopic study of intercalated cationic dyes into montmorillonite with different layer charge

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Modified montmorillonites with cationic dye exhibit unique optical properties. These novel materials enable many applications in photochemical and photophysical branch [1]. Generally, cationic dyes form the aggregates on surface and/or in the interlayer of montmorillonite. Dye loading and layer charge of montmorillonite are control elements of dye aggregation [2].

In this study a Ca^{2+}-montmorillonite with high (SAz) and reduced charge (RC-SAz(210)) were used for the preparation of cationic dye/montmorillonite complexes. The RC-SAz(210) was prepared from parent material (SAz) by Li^+ saturation and subsequent heating at 210°C. The exchanges in fluorescence and Vis electron spectra of the complexes were observed.

Vis absorption spectra of four cationic dyes (CD), i.e. methylene blue (MB), crystal violet (CV), nile blue (NB) and rhodamine B (RB) were measured. The percentage distribution of non aggregated and aggregated CD species in variously concentrated aqueous solution was calculated using equilibrium stepped aggregation constants K_n. The study showed that nile blue forms the higher aggregates in aqueous solution already at relatively low concentration compared with the other tested dyes.

Vis electronic spectroscopy and X-ray diffraction analysis revealed that cationic dye in fully intercalated CD/SAz complex is located in the interlayer of montmorillonite mainly in form of higher aggregates. The higher aggregates of dye are effective quenchers of fluorescence hence these complexes exhibit a very low fluorescence intensity. The reduction of montmorillonite layer charge and low dye loading in the CD/RC-SAz(210) complexes cause suppression of dye aggregation and huge increase of fluorescence (Fig. 1).

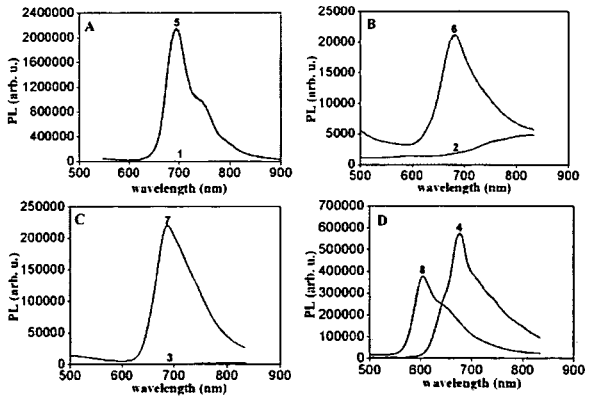

Fig. 1: Fluorescence spectra of fully intercalated CD/SAz complexes (spectra 1, 2, 3 and 4) and spectra of CD/RC-SAz(210) prepared by 10% dye loading (spectra 5, 6, 7 and 8). A- Methylene blue; B- Crystal violet; C- Nile blue; D- Rhodamine B.

[1] Bujdák, J. (2006) *Appl. Clay Sci.*, **34**, 58-73. [2] Klika, Z. et al. (2009) *J. Colloid Interf. Sci.*, **339**, 416-423.

Wettability of clay mineral surfaces – molecular dynamics study

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Wetting properties of soil and soil components affect a wide variety of soil processes including infiltration, preferenti al flow and surface runoff [1]. The wetting ability of a solid surface is mainly determined by its chemical composition and structure and is directly related to the solid surface free energy [2]. The solid-liquid contact angle method is often used to characterize wettability of surfaces and to determine its surface energy. In soil chemistry, contact angle measurements are influenced by many factors because of the heterogeneous and complex nature of soil particles. Therefore, it is important to know how individual soil components behave with respect to polar liquids like water.

Clay minerals represent an important inorganic part of soil mineral phases and significantly affect overall properties of soils. Owing to compositional variability ad structural complexity various clay minerals behave considerably differently with respect to wetting.

In order to elucidate structural and compositional factors affecting hydrophilic/hydrophobic character of clay minerals we studied interactions of water nanodroplets with basal surfaces of selected clay minerals (particularly kaolinite and phlogopite) by means of classical molecular dynamics simulations at room temperature. From the behaviour and shape of the nanodroplet it was possible to characterize hydrophobic/hydrophilic character of studied surfaces. In case of the kaolinite octahedral surface formed from surface hydroxyl groups, the water droplet was completely spread and a monomolecular network of hydrogen-bonded water molecules was formed. In opposite, the tetrahedral surface, which is formed from basal oxygen atoms, is less interacting with the water nanodroplet and the shape of the droplet is partially preserving. The molecular simulations clearly showed a difference between both basal surfaces of kaolinite. While the octahedral surface is strongly hydrophilic, the tetrahedral surface has partially hydrophobic character. Structural and energetic aspects of both surfaces are obtained as well.

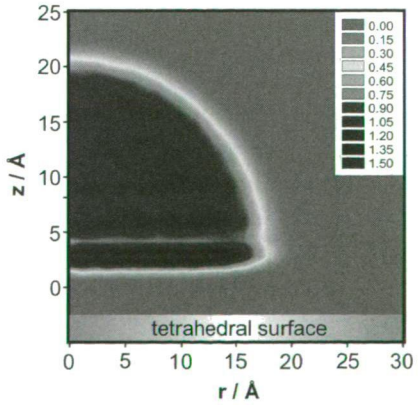

Fig. 1: Water density profile (in g/cm^3) of water nanodroplet on tetrehadral kaolinite surface. (500 water molecules, 2 ns MD, 300K).

[1] Anderson, M.A. et al. (1995) *Soil Sci.*, **160**, 111-116. [2] Bachmann, J. et al. (2000) *Soil Sci. Soc. Am. J.*, **64**, 564-567.

Organic modified montmorillonite supported cobalt catalyst for Fischer–Tropsch synthesis

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The Fischer-Tropsch synthesis (FTS) is a process that converts syngas into mixtures of higher molecular weight hydrocarbons. Supported cobalt catalysts are the preferred catalysts because of their high F-T activity, high selectivity for linear hydrocarbons, low activity for the water gas shift reaction, and relatively lower cost. In this paper, organically modified montmorillonite as a novel support is first applied to cobalt-based Fischer-Tropsch synthesis.

Normally, XRD is a good method for identification and characterization of the F-T active phases. However, only the in-situ XRD shows reliable data about the structure of cobalt active phases present in the reduced and working catalysts because of easy reoxidation of cobalt species in the air. Our results show that ex-situ XRD was also an effective method for the active phase identification of the Co/ OMMT catalysts after F-T synthesis (see Fig. 1), because there was no reoxidation on the catalysts after F-T reaction due to the formation of carbon protective layer outside the metallic cobalt, which was from decomposing of the organic component inside the layer of montmorillonite. This retains precious information about cobalt dispersion and reducibility under the FT reaction conditions.

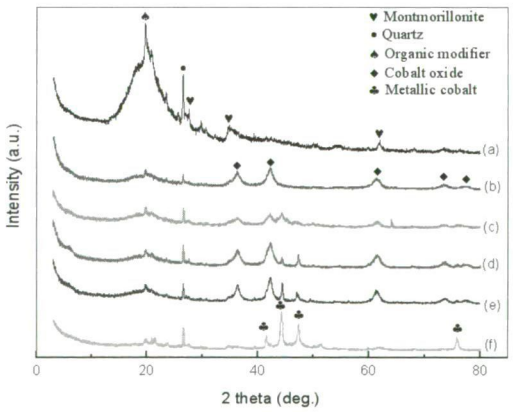

Fig. 1: XRD patterns of the samples (a: organically modified montmorillonite (OMMT); b: Co/ OMMT; c–e: Co/ OMMT catalysts after different Fischer-Tropsch reaction conditions).

Table 1: Catalytic performance of catalysts for F-T synthesis reaction

Sample	CO conversion (%)	CH_4 selectivity (%)	C_2-C_4 selectivity (%)	C_5^+ selectivity (%)
c	24.48	19.98	6.67	73.35
d	14.65	16.53	0.78	82.69
e	26.27	7.08	2.45	90.47
f	15.84	94.28	1.69	4.03

The data in table 1 show that the C_5^+ selectivity was improved with the increase of metallic cobalt content in catalysts c–e. The C_5^+ selectivity of the catalyst f was the worst on the highest metallic cobalt content, due to the catalyst producing more carbon under these conditions.

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A molecular dynamics simulation studies of ethylene glycol intercalated in smectites

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Intercalation of ethylene glycol in smectites is widelly used to discriminate smectites from other clays. This technique has been known since pionnering work of MacEvan [1], however still little is known about the structure of ethylene glycol between smectite sheets. The work by Reynolds [2] gave some insights into the structure, hovewer since that time no significant input into the understanding of this structure has been done.

Molecular dynamics simulations allow to find that the structure proposed by Reynolds [2] should be a bit different. Ethylene glycol forms two distinct layers between sheets, but ions forms inner and outer sphere complexes, not only the outer ones as it was described in [2]. Moreover water in this structure was found not to form distinct layers but is rather spread out and concentrated around ions. There is also no tendency to form water bridges between ions, water and ethylene glycol.

Molecular simulations were carried out using the DLPOLY computer program using CLAYFF and CVFF force fields to describe clay and ethylene glycol, respectively.

[1] MacEwan, D.M.C. (1946) *J. Soc. Chem. Ind.*, **65**, 298-304.
[2] Reynolds, R.C. (1965) *Am. Mineral.*, **50**, 990-1001.

Formation of a second-staged alkylammonium-sericite complex

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The intercalation dynamics of layered materials, such as graphite, clays, and transition-metal dichalcogenides, has been reported in detail, both experimentally and theoretically. In particular, the phenomenon of staging has generated a large amount of interest in these materials. Staging is a process by which layered host materials intercalate guest compounds. A staged layered compound has a regularly repeating series of interlayers, alternating periodically between an intercalated layer and non-intercalated layer. In the present study, the staging phenomenon was investigated for the organic/sericite complexes.

We have conducted ion exchange experiments using sericite (SE) and dehydrated sericite (dhSE) with dodecylammonium (DDA) solutions of various initial concentrations (7.3, 21.9, and 73.3 mM, corresponding to DDA^+/K^+ mole ratio = 1.0, 3.0 and 10.0, respectively), at 70°C. The dhSE sample was prepared by dehydration of a SE powder (medium particle diameter: 7.8 μm) at 800°C for one hour [1]. The staging phenomenon was studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and infrared absorption spectra. Typical XRD patterns of DDA-SE and DDA-dhSE prepared by ion exchange with a low DDA concentration (DDA^+/K^+ = 1.0), are shown in Figure 1. In the case of the SE complexes, two separated phases, 1.0 and 2.3 nm, were obtained, which were ascribed to the non-intercalated layers, and vertical (perpendicular to the layers) orientations of the incorporated DDA, respectively. On the other hand, in the case of the dhSE complexes, a large basal spacing of 3.3 nm was observed (Fig. 1b). The 3.3 nm basal spacing is close to the sum of the basal spacing for the vertical (perpendicular to the layers) orientations and that for the non-intercalated layers, so it can be interpreted as regular alternation of the 2.3 nm layer and the 1.0 nm layer, exhibiting c =3.3 nm supercell ("1:1 ordered interstratifications" or "second-staging").

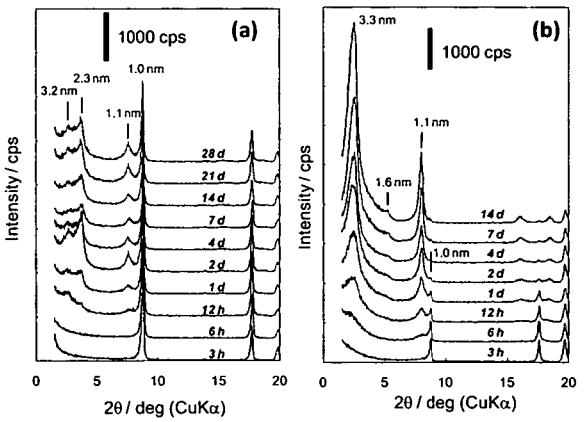

Fig. 1: XRD patterns of (a) DDA-SE and (b) DDA-dhSE complexes prepared by ion exchange with DDA^+ (DDA^+/K^+ mole ratio = 1.0) at 70°C for various duration times.

[1] Tomita, K. & Dozono, M. (1972) *Clay. Clay Miner.*, **20**, 225-231.

Alteration mineralogy, geochemistry and genesis of volcanic rocks of the Hasandağ area (Giresun), NE Turkey

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The Eocene subvolcanic and volcanic rocks of the Hasandağ (Giresun) area in the eastern Pontides (NE Turkey) have undergone several stages of hydrothermal alteration. The rocks of the area comprise andesitic flows, andesitic pyroclastic rocks, phreatomagmatic breccia, andesite dykes and granodiorite-syenogranite intrusions. Development of phreatomagmatic breccias was related to penetration of silica-rich hydrothermal fluids along fractures. Consequently, silicification and scarce argillisation are widespread main types of hydrothermal alteration in the area. These units were studied via standard petrography, reflected-light polished-section microscopy, X-ray diffractometry (XRD), scanning electron microscopy (SEM-EDX), and geochemical analysis. Alteration of plagioclase and iron-oxidation in amphibole and biotite are widespread. Development of silicification, advanced argillisation (alunite±kaolinite), argillic (smectite±illite) and propyllitic zones (chlorite±sericite±calcite) – associated with decreasing alunite±kaolinite and some increase in chlorite±sericite±calcite from the central to the outer part of the study area – indicate acidic hydrothermal activity. The operation of these hydrothermal processes is also evidenced by geological and geochemical determinations. In the study area, pyrite, visible gold and native elements were all determined via ore microscopy. The pyrite is of three types; type 1 is coeval with the host rocks, the other two types of pyrite occurrence developed via epithermal activity. Pyrite crystals are 1-1000 microns, gold 2-15 microns, and native elements 1-20 microns in size. Hypogene minerals include goethite and lepidocrocite. Based on geochemical analyses, the trace- and rare-earth element patterns of the volcanic rocks (except the phreatomagmatic breccia) are similar to each other, and all resemble arc volcanic rocks. Thus, geological, petrographic, mineralogical and geochemical data on these Eocene volcanic rocks and their hydrothermally altered equivalents indicate an epithermal system.

Geology, mineralogy and depositional environment of the Pliocene Cappadocian Volcanic Province, Yeşilhisar (Kayseri, central Anatolia, Turkey)

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Pliocene alluvial and lacustrine deposits characterize the so-called Kısladağ Formation of the Cappadocian Volcanic Province (central Anatolia). The Güzelöz Plateau (Yeşilhisar) in the central part of the Cappadocian Volcanic Province contains many ignimbrite levels, andesite, and basalt intercalated with paleosols, calcretes, lacustrine carbonates, fluvial sediments, diatomaceous clayey sediments and pyroclastic sedimentary levels. The presence of root traces and remnants, paleosols, and calcrete indicate fluvial and shallow-lake environments. These environments are dominated by feldspar, quartz, calcite, opal-CT, serpentine coexisting with smectite, illite and accessory palygorskite. Smectite predominates in paleosols and calcrete units. Development of microsparitic to sparitic calcite cement between irregular clay nodules in paleosol and calcrete samples, and dog-tooth-type sparitic calcite crystals in fractures and cracks, indicate alternating dry and wet periods, that resulted in the development of paleosols and calcretes. The $\delta^{18}O$ values of the calcretes range from –9.13 to –10.69 ‰ PDB, reflecting their formation under the influence of meteoric water. $\delta^{13}C$ values of the calcretes are between +4.97 and +3.00, and may have been related to drought conditions, increase in C_4 biomass, and decrease in atmospheric CO_2 concentrations below a threshold that favoured C_3 plants [1]. $\delta^{18}O$ and $\delta^{13}C$ isotope values from limestone samples vary between –9.81 to –10.71 and 1.85 to –4.84 ‰ PDB, respectively. Negative $\delta^{18}O$ values and low [MgO/(MgO+CaO)] ratios indicate low salinity and freshwater influx into the lake [2]. The negative calcite $\delta^{13}C$ values of the limestones clearly indicate a biogenic origin, lake expansion and increased through-flow conditions, whereas positive values indicate lake contraction, decreased through-flow conditions and biogenic activity. The Pliocene interval, represented by paleosols, calcretes and lacustrine carbonate rocks in Cappadocia region, is of special interest insofar as it included global changes in vegetation (C_3 to C_4 ecosystems) and drought-wet fluctuations.

[1] Cerling, T.E. et al. (1997) *Nature,* **389**, 153-158. [2] Dutkiewicz, A., Herczeg, A.L. & Dighton, J.C. (2000) *Chem. Geol.*, **165**, 309-329.

Investigation of magnetic and adsorption properties of natural and magnetic sepiolite

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In this study, we investigated a sepiolite sample obtained from Sivrihisar region (Eskisehir-Turkey). Firstly, instrumental characterization of the clay sample was performed by various techniques such as XRD, XRF, TG/DTA, SEM. Magnetic modified forms of clay minerals have been prepared and then adsorption and magnetic properties of unmodified and modified clays were compared with each other. The magnetic modified forms of clay samples have been prepared in the following way: The fractions of clay samples that have dimensions smaller than 63μm have been separated by sieving. They were mixed and intensively ground with powder forms of magnetite in a mortar. The resulting powder mixture was slowly heated up to 950°C at 1°C/min and maintained at this temperature for 6 hours. The solid sample was cooled and washed with de-ionized water until no Cl^- ions were detected in the eluted water, and then dried at 80°C during 16 hours [1].

The adsorption isotherms of nitrogen gas on natural and magnetic modified clays have been obtained by means of Quantachrome Nova 2200E model high speed gas analyzer. The magnetic properties of the samples have been determined by means of LakeShore 7307 model Vibrating Sample Magnetometer.

Table 1: Comparison of specific surface areas, average pore diameters for natural and magnetically modified clays

Forms of Clay	Specific Surface Area(m^2/g)	Average Pore Diameter (Å)
Sepiolite	293.52	84,38
Sepiolite-Fe	68.34	92,17

As shown Table 1, the specific surface areas of magnetically modified clays are smaller than the specific surface areas of natural clays. The average pore diameters of magnetically modified clays are greater than the average pore diameters of natural clays.

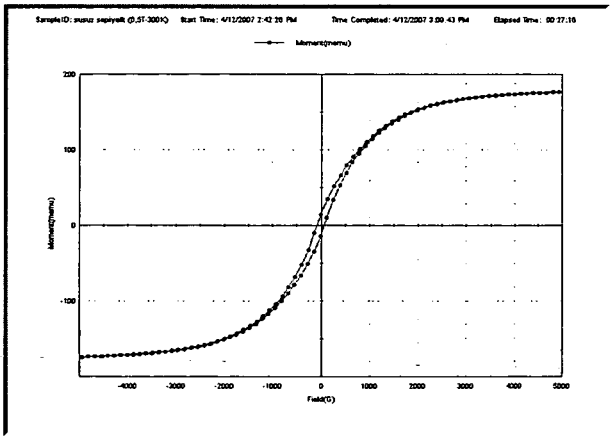

Fig. 1: Magnetization versus applied field curve at room temperature (max. magnetic field 0.5T) for the magnetic modified sepiolite.

The magnetic clay sepiolite is characterized by the maximum magnetization value of 176,4 memu (Fig. 1). Similar results could be obtained for other natural clays and porous materials.

[1] Čapek, L. et al. (2005) *Micropor. Mesopor. Mat.*, **80(1-3)**, 279-289.

Hungarian contribution to mineralogy and geology of clays

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The Hungarian Clay Minerals Group was founded in 1960. On the occasion of the *50th anniversary* the main results of the Hungarian clay research in the field of earth sciences is reviewed.

A *general textbook* on clay minerals was published by the founder of the Clay Group, professor Nemecz. In a broader sense the fundamental books of Bárdossy on bauxites belong to the clay research. Soil clay minerals were discussed in the textbooks of Stefanovits, Szendrei and Nemecz, and recently by Nagy and Kónya.

Specific clay minerals. The famous illite mineral of Füzérradvány, the "second illite of the world" was described by Maegdefrau & Hofmann as early as 1937 and later reviewed by Nemecz & Varjú. Weiszburg and E. Tóth contributed much to the chemical systematics of celadonite, glauconite and "Fe-rich montmorillonite" series. Serpentine minerals were extensively studied by Erdélyi and in the last years by Dódony (structural analyses of antigorite and polygonal serpentine).

Determinative methods in clay mineralogy. A method of quantitative analysis by X-ray diffraction was introduced by Náray-Szabó. A special apparatus for thermal analysis called "Derivatograph" was developed by Paulik & Paulik. Atlas of thermal analysis was created first by Földvári-Vogl. The application of the method was later continued on a high level by M. Földvári.

Soils and rocks. Stefanovits and Dombóvári published the map of clay minerals in Hungarian soils. Red clays, mostly relict fossil soils were studied by Bidló. Fekete published book on recent tropical soils. *Fossil lake sediments* of basaltic craters were recognised by Solti and analysed by Földvári, Barna and others. Mostly rhyolite-related bentonite deposits of the Carpathian Basin were studied by Kovács-Pálffy.

Lithostratigraphic application. Clay minerals of Hungarian sedimentary formations were systematically characterised by Viczián. Today this line is continued by Raucsik, Varga and Szakmány. The *diagenetic transformation* of smectite to illite was widely applied for CH prospecting by Viczián, J. Mátyás and others. The *very low grade metamorphic stage* is studied by Árkai and his co-workers M. Tóth, Judik etc. He introduced the parameter "chlorite crystallinity" (Árkai index), studied index minerals, applied textural analysis etc. His studies extended to Hungary, the Swiss Alps, and to SE-Europe.

Zones of *hydrothermal alteration* in the Tokaj Mts. were first recognised by Széky-Fux, later intensively studied by Nemecz and Varjú and recently by Molnár. *Economic clay deposits* were studied for several decades by E. Mátyás and Zelenka, their colloidal properties by Juhász, Szántó and their students. Model experiments of *environmental pollution* by heavy metals are carried out by Németh. Clay liners for communal *waste depositories* were developed by Szabó. Pelitic host rocks for radioactive waste depositories are studied in Mecsek Mts.

Mineralogical and chemical composition of clayey deposits in caves

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Clay deposits in caves are quite specific in nature due to their origin and therefore are not well investigated.

For the purposes of this research samples from: Sumgan-Kutuk Cave (Bashkortostan, the Urals), Kapova Cave (Bashkortostan, the Urals), Canyon Cave (Krasnodar region, the Caucasus), Voronya Cave (Abkhazia, the Caucasus) and Cascade Cave (the Crimea, Ai Petri) have been considered.

Analysis of particle size distribution showed that in all the caves studied there are two types of deposits: sandy silt, where percentage of clay fraction (less than 0.002mm) is 3.7% with predominant silt fraction (0.002 to 0.01mm) of 50-75%; and clayey silt where the percentage of clay fraction is 12.6%, with silt (0.002 to 0.05mm) being dominant (70-80%).

The mineral composition of the clay fraction is dominated by illite-smectite interlayerings (35-50%) with predominant illite layers, kaolinite (4-10%), chlorite (approximately 6%), smectite (approximately 1%), calcite (approximately 1%), iron hydroxides (approximately 1%). The amount of detrital quartz reaches 40% in the <0.002 mm fraction.

Further chemical analysis of the alumo-silicates from the clay fraction, carried out using a Jeol JSM-5300 scanning electron microscope equipped with EDS, showed that: *Illite* has high potassium content and characterized by 52.27% SiO_2, 26.49% Al_2O_3, 3.92% Fe_2O_3, 4.90% MgO, 3.58% of CaO, 2.44% Na_2O and 6.40% of K_2O. *Chlorite* is represented by the magnesium type and contains 31.23% SiO_2, 27.43% Al_2O_3, 5.89% Fe_2O_3, 29.05% MgO, 0.51% CaO, 4.91% Na_2O and 0.99% K_2O. *Smectite* is defined by high iron content and has 32.35% SiO_2, 22.84% Al_2O_3, 32.13% Fe_2O_3, 5.81% MgO, 2.86% CaO, 2.09% Na_2O and 1.91% K_2O. The clay minerals from the studied deposits have similar chemical compositions, regardless of the sampling site.

The chemical composition of clay fraction of the main type deposits is presented by: SiO_2 55.81%, Al_2O_3 27.41%, Fe_2O_3 4.94%, MgO 3.44%, CaO 1.35%, Na_2O 2.27%, K_2O 4.78% for clayey silt; and SiO_2 54.19%, Al_2O_3 27.73%, Fe_2O_3 3.66%, MgO 5.38%, CaO 0.90%, Na_2O 2.36%, K_2O 5.77 for sandy silt.

As shown in Fig. 1, REE spectrum of clay fraction in sandy and clayey silt (average of all samples) is quite similar.

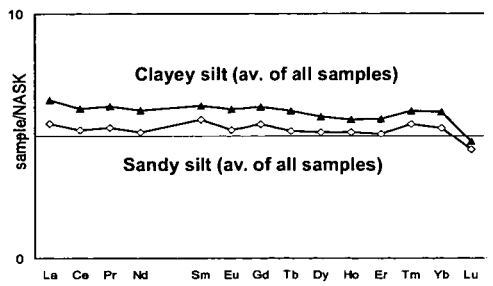

Fig. 1: REE spectrum of clay fraction in sandy and clayey silt (average of all samples).

Taking into account the results of mineralogical and chemical composition of clayey deposits from caves in Caucasus, Crimea, and the Urals, the following conclusion can be made. Clayey deposits from all considered caves are represented by two types of sediments (sandy silt or clayey silt) that show differences in the micro-facies of their deposition environment. Mineralogical composition of clay fraction is similar for all analyzed samples, with predominant illite-smectite mixtures with a percentage of smectite layers < 35%.

Montmorillonitic alteration of tourmaline from the Quintos de Baixo pegmatite, Borborema Pegmatite Province, NE Brazil

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Tourmaline is a common boron-rich mineral in granitic pegmatites [1]. It is resistant to weathering and typically occurs as a detrital mineral in sedimentary rocks and soils. However, tourmaline in pegmatites may be partially altered to various aluminous minerals. Alterations are mostly associated with late magmatic and hydrothermal fluids [2].

Tourmaline from the Quintos de Baixo pegmatite, Borborema Pegmatite Province, NE Brazil, displays zonal structure with Li-Al-rich core (elbaite) and Fe-rich rim (schorl). The core is frequently altered to clay minerals. The matrix between tourmaline crystals comprises clay minerals as well. According to X-ray powder diffraction (XRPD) analysis the principal clay mineral is montmorillonite with cation exchange capacity (CEC) of 75.5 ± 0.4 mEq/100g.

The following reaction illustrates the breakdown of tourmaline (elbaite) into Li-montmorillonite:

$$Na(Li,Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4 + 5H_4SiO_4 + 3H^+ \leftrightarrow 3[Al_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2]Li_{0.33} + 3H_3BO_3 + 2Li^+ + Na^+ + 6H_2O \quad (\Delta_rG^0 = -69.7 \text{ kcal/mol})$$

The reaction requires increased activity of H_4SiO_4 and points to the influence of late magmatic or hydrothermal fluids (Fig. 1). Alternatively, the weathering of spodumene can represent an important source of montmorillonite:

$$7LiAlSi_2O_6 + 6H^+ + 6H_2O \leftrightarrow 3[Al_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2]Li_{0.33} + 3H_4SiO_4 + 6Li^+ \quad (\Delta_rG^0 = -2.6 \text{ kcal/mol})$$

Gibbs free energies for above mentioned reactions (Δ_rG^0) have been estimated according to the thermodynamic data published by Woods & Garrels [3], Tardy & Garrels [4] and Ogorodova et al. [5].

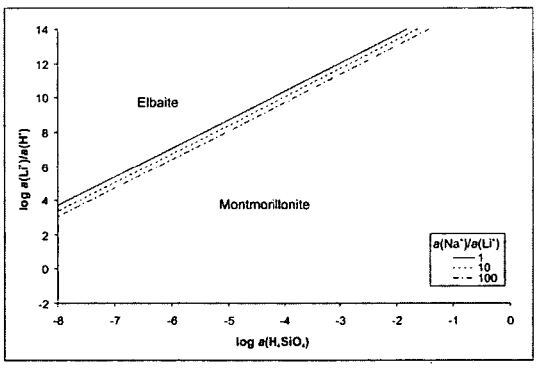

Fig. 1: Logarithmic activity diagram, constructed for standard conditions (1 bar, 25°C).

[1] London, D. et al. (1996) *Rev. Mineral.*, **33**, 299-330. [2] Ahn, J.H. & Buseck, P.R. (1998) *Am. Mineral.*, **83**, 535-541. [3] Woods, T.L. & Garrels, R.M. (1987) *Thermodynamic values at low temperature for natural inorganic materials.* Oxford University Press, New York. [4] Tardy, Y. & Garrels, R.M. (1974) *Geochim. Cosmochim. Ac.*, **37**, 1101-1116. [5] Ogorodova, L.P. et al. (2004) *Thermochim. Acta*, **419**, 211-214.

The mineralogical and petrographic study of zeolitic tuffs around Karamürsel, NW Turkey

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Paleocene pyroclastic rocks of the volcano-sedimentary sequence which disconformably overlie Triassic conglomerates and sandstones underwent locally a strong alteration in the area around Karamürsel, NW Turkey (Fig. 1).

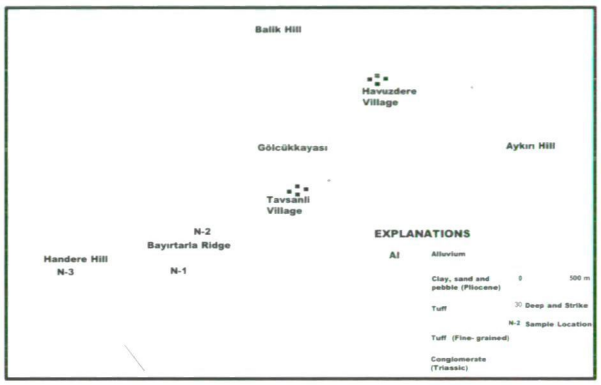

Fig. 1: Geological map of the study area [3].

Volcanic tuffs, which have the composition from andesite to rhyolite, underwent diagenetic alteration. Zeolites (clinoptilolite, heulandite), clay minerals and micas (smectite, illite, celadonite, glauconite and biotite), siliceus minerals (opal-CT, quartz), carbonate minerals (calcite) and feldspars are authigenetically formed. Thermal stability studies indicate that the zeolite types are clinoptilolite and heulandite-2 (Ca-clinoptilolite). Clinoptilolite is stable at 550°C. Si/Al ratios of selected 3 zeolite samples range from 4.70 to 5.84. Heulandites have been distinguished from iso-structural clinoptilolites on the basis of their Si/Al ratios, heulandites having Si/Al <4 and clinoptilolites having Si/Al>4 [1,2]. XRD studies indicate that Karamürsel samples contain typical heulandite with d(060) spacing higher than 1.51Å (Fig.2). Glauconite (Al-glauconite) identified with celadonite-glauconite distinguishing methods was found to be a mixed-layer mineral.

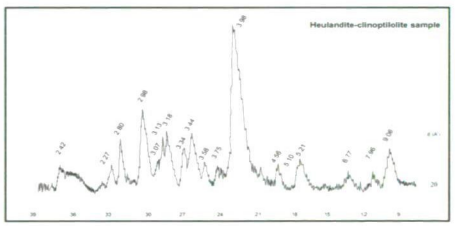

Fig. 2: XRD pattern of heulandite-clinoptilolite bearing tuff

Cationic values were recalculated on the basis of 72 oxygen atoms, providing the following average half unit cell composition of the glauconite: $K_{0.53}(Fe_{0.89}, Al_{0.53})$ $(Mg_{0.48}, Fe_{0.17})$ $(Si_{3.65}\ Al_{0.35})\ O_{10}\ (OH)_2$.

[1] Coombs, D.S. et al. (1997) *Can. Mineral.*, **35**, 1571-1606. [2] Esenli, F. et al. (2005) *Geol. Croatica*, **58/2**, 151-161. [3] Uz, B. et al. (1995) *Geosound*, **27**, 135-147.

Effects of dry grinding on kaolinite powders

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Particle size reduction in clays and clay minerals is produced by grinding, which plays an important role in the physicochemical properties of the resulting powders and in the further processing steps. Most papers report that short-time milling of kaolinite flakes causes fracturing along the basal planes coupled with an increase of the specific surface. Several author teams examined the mechanochemical effects of grinding of kaolinite on its structure and thermal behavior and subsequent thermal transformations. Physicochemical changes of the material were observed after applying grinding friction forces, such as present in vibratory, oscillating, and planetary mills [1]. The effects of different times of dry grinding using ball-milling on the structure of kaolinite powders KGa-1 and KGa-2 from Georgia showed that the peak temperatures of the endothermic DTA effects shifted slightly to lower temperatures as grinding time increased. The exothermic peaks were affected only after longer grinding periods [2].

Well-ordered (KGa-1) and low-ordered (KGa-2) kaolinite powders from Georgia were compared after 15 min jet- and ball –milling. The surface area increased, the particle size distribution and the weight loss on heating were different in dependence on the type of milling. he DTA effects did not change after milling.

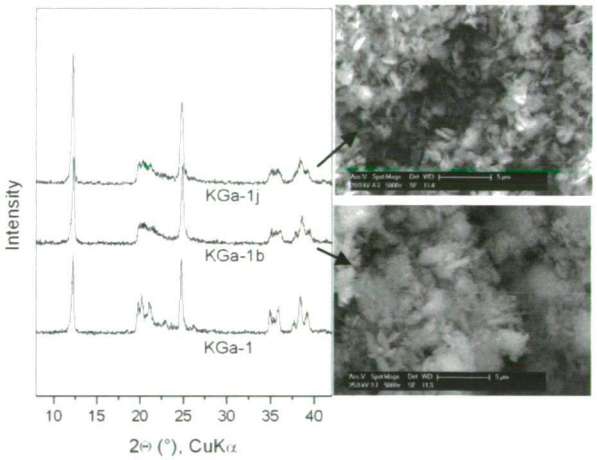

Fig. 1: XRD patterns of KGa-1, ball-milled KGa-1b, jet-milled KGa-1j and SEM micrographs of KGa-1b and KGa-1j.

The X-ray powder diffraction (XRD) patterns (Fig. 1) show the loss of resolution of the peaks near 21.5 °2Θ which is some evidence for a small disorder in the ordered phase [3].

Acknowledgements: This work was supported the Czech Grant Agency (projects GA ČR 105/08/1398 and 205/09/0352).

[1] Aglietti, E.F. et al. (1986) *Int. J. Miner. Process.*, **16**, 125-133. [2] Sánchez-Soto et al. (2000) *J. Am. Ceram. Soc.*, **83**, 1649-1657. [3] Reynolds, R.C.,Jr. & Bish, D.L. (2002) *Am. Mineral.*, **87**, 1626-1630.

Detailed clay mineralogy of a continuous, marine Tr/J boundary section at Kendlbachgraben, Austria

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A marine Triassic/Jurassic boundary section is exposed at Kendlbachgraben in the Northern Calcareous Alps. It is located in the Eiberg basin, similarly to the Kuhjoch section, which has been chosen as the Global Stratotype Section and Point for the base of Jurassic.

Selected samples of the Kendlbachgraben section were investigated for clay mineral species determination. Routine oriented specimen diagnostic procedures were followed. Cation exchange for Mg and K was performed. Peaks of X-ray diffraction patterns were resolved by deconvolution procedures. Observed species are ~15 Å smectite (Mg>Fe), together with vermiculite (K-bearing) and chlorite (Fe>Mg) (14,2–14,5Å), illite and kaolinite. The identified "14Å type" minerals are Mg-dominant, with varying Fe, K and Ca content. Chlorite is evident only after heating to 560°C and diminishes upwards in the section. Kaolinite shows a decrease in quantity and degree of crystallinity upwards in the section. Cation exchange and glycerol saturation indicates the mixing of high and low layer charge smectites, with the dominance of the high-charge type. Vermiculite is of the low layer charge, expanding type.

The lowermost sample of section (KB1) has a very different clay mineral content compared to the other samples. It contains dominantly high-charged smectite and also vermiculite. These clay minerals may be formed by the alteration of mafic and ultramafic rocks. Upwards in the section (KB8) smectites has a Ca–Na enrichment and vermiculite (chlorite) becomes dominant. In the boundary shale the clay mineral distribution is the following: kaolinite≥ illite + muscovite >> smectite. This suggests weathering under humid climate, and intensive terrigenous input. Above the boundary interval the clay mineral pattern changes to illite + muscovite >> kaolinite >> smectite, which corresponds to a less humid, mainly moderate climate.

Some pale-green, opaque or slightly transparent grains, 70–80 μm in size, are found in the topmost layer of the Triassic Kössen Formation (KB1). Their shapes vary from the perfectly spherical (Fig. 1) to the angular. They are identified as illite/aluminoceladonite, their average EDX composition is $K_{0.49}Na_{0.08}Ca_{0.07}Mg_{0.65}Fe^{2+}_{0.07}Al_1Fe^{3+}_{0.41}[Al_{0.4}Si_{3.6}O_{10}(OH)_2]$. They presumably represent alteration products of volcanic material, on the basis of their shape and size. Most probably the rounded grains were altered from volcanic glass spherules.

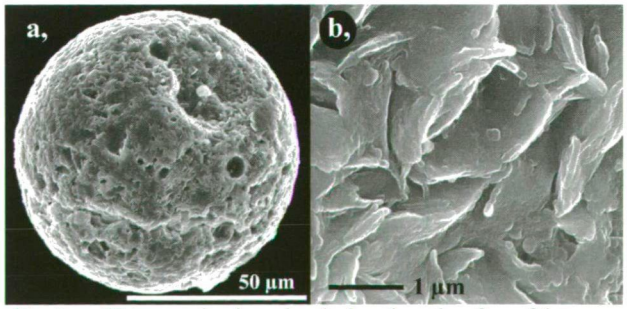

Fig. 1: a, SE image of a clay spherule. **b,** enlarged surface of the same spherule.

Archaeometrical investigation on glass beads coming from Villanovian excavations in Bologna (Italy)

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Excavations performed in seventies around the actual fair area of Bologna brought to light remains of VII-VIII century civilizations [1]. The archaeological work allowed the collection of a large number of objects which clearly indicate the presence of a large Villanovian village. The archaeological excavations on the annexed necropolis are still in progress and the study is unpublished. The necropolises of Bologna Fair are dated from 800 to 750 BC (Villanovian II) and from 750 to 680 BC (Villanovian II).

Several glass beads were recovered during the excavations. Twenty-seven blue, turquoise, black and dark green glass beads were selected and analysed. The chemical analyses of major and minor elements were obtained by WDS-EMPA, while the analyses of eventual opacifiers dispersed in the matrix were carried out with the combination of XRD and SEM-EDS observations.

The chemical data of the samples allow identifying a group of four beads characterized by a mixed alkalies composition, typical of the Final Bronze Age production found in [2,3]. All the other samples show low levels of K_2O (<2 wt%) and rather high Na_2O (>15 wt%). Some of these samples can be classified as natron-based glass, while for a number of beads the classification is not straightforward, since they contain, along with low K_2O, a high amount of MgO (about 3 wt%). These low potassium high magnesium glasses show, in addition, extremely high levels of Al_2O_3. These results indicate that the glass found in this site derive at least from three different melts. Regarding the opacity of the samples, in most of the cases the effect is due to the dark colour of the glass (i.e. in blue, dark green and black beads) which prevent obliterate the transmission of light. Only in the turquoise samples, crystalline particles of calcium antimonate were found.

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An advanced methodology for Remote Operation Vehicle magnetic survey to delineate buried targets and estimate medium magnetization

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A role of iron in the Earth evolution and investigation of the present environment is extremely important (e.g., [1]). Magnetic survey is one of most applied geophysical method for searching and localization of any objects with contrast magnetic properties (for instance, in Israel detailed magneric survey has been succesfully applied at more than 40 archaeological sites [2]). However, land magnetic survey cannot be performed in swampy and karstic areas, districts with dense natural growth and in some other districts. Conventional airborne magnetic measurements are limited by a flight level, too high velocity of flight, heightened danger for the aircraft crew by low-altitude survey, and financial considerations. At the same time the new Remote Operation Vehicle (ROV) generation – small and maneuvering vehicles – can fly at levels of few (and even one) meters over the earth's surface (flowing the relief forms or straight) with simultaneous precise magnetic field measurements. Such geophysical investigations should have an extremely low exploitation cost. Finally, measurements of geophysical fields at different observation levels could provide new unique geological-geophysical information [2].

The developed interpretation methodology for magnetic anomalies advanced analysis [3] may be successfully applied for ROV magnetic observations. This methodology includes: (1) non-conventional procedure for elimination of secondary effect of magnetic temporary variations, (2) calculation of rugged relief influence by the use of a correlation method, (3) estimation of medium magnetization, (4) application of various logical-heuristic and informational algorithms for revealing small anomalies against noise background, (5) advanced procedures for magnetic anomalies quantitative analysis (they are applicable in conditions of rugged relief, inclined magnetization, and an unknown level of the total magnetic field for the models of thin bed, thick bed and horizontal circular cylinder; some of these procedures demand performing measurements at two levels over the earth's surface), (6) advanced 3D magnetic-gravity modeling for complex media, and (7) development of 3D physical-geological (or magnetic-geological) model of the studied area. ROV observations also permit to realize a multimodel approach to magnetic data analysis [4]. Results of performed 3D modeling confirm an effectiveness of the proposed ROV low-altitude survey.

Khesin's methodology [3] for estimation of upper geological section magnetization consists of land magnetic observations along a profile disposing under inclined relief with the consequent data processing (this method cannot be applied at flat topography). It was suggested that integrated ROV straight and inclined observations will help to obtain parameters of the medium magnetization even over the flat relief.

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Mineralogy and archaeometry: fatal attraction

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The difficult and fascinating relationship between archaeometry and mineralogy continuously offers challenges and topics for research, though it is often troubled by the sectorial organization of academic structure, at present also severely limited by budgetary cuts [1,2]. The existing competition between traditional academic disciplines in the field of cultural heritage is often pernicious and poorly effective as far as information and knowledge transmission is concerned. The continuity in the employment of highly trained researchers and the poor strategy in the data publication are issues of great concern. Centralised research facilities could have a leading role in the management of multi-disciplinary research, though they have a limited practical effect in a shrinking budget world.

Within this frame, disciplines such as mineralogy and petrology, intrinsically used to deal with complex systems, found new natural areas of applications in cultural heritage materials. Archaeometry-oriented applications rose from the status of exotic studies to widely diffused areas of research within the last decade, partly because of the fascination of the involved problems, and partly because of the limited funding in the traditional fields of research. It is argued that mineralogy as a discipline at the crossroad between the core Earth Sciences, crystallography, materials science, and geochemistry might be a key area of innovation for cultural heritage studies.

A few case studies will be discussed to convey a personal view of mineralogical applications within the broader context of cultural heritage investigations [3]. Key issues are: the use of combined techniques for the characterization of complex systems, the optimization of non-invasive techniques, the appropriate use of data bases in archaeometry.

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On the origin of the green colour of archaeological bone artefacts of galloroman period

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Bone artefacts of the Gallo-Roman period have been discovered in the Reims city in 2004 in a place that was identified as a workshop dedicated to bone objects. Among the bone pieces, some of the finished objects are coloured in green by copper. However, the colouration cannot be due to a long contact with a metallic object made of bronze or copper. The understanding of the origin of this colour is very important to decipher if the colouration was made intentionally and to get knowledge about the processes developed by the craftsman.

In this work, two archaeological green objects from the site of Reims, one archaeological bone coloured by contact with a metallic object and fresh bones coloured in the laboratory are compared. Infra-red spectroscopy was used to get information on the organic part of the samples while X-ray diffraction allowed us to characterize the crystalline part. X-ray absorption spectroscopy at the Cu K-edge was used to obtain information about the environment of Cu in the artefacts. Finally, SEM-EDS experiments have been used to localize the copper in the bone structure.

Ancient metals provenancing: a geochemical database of Alpine copper mines

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The provenance of ore minerals used in prehistoric and historic times for copper smelting and extraction is one of the basic questions that archaeologists pose to modern analytical archaeometry [1]. To aid metal provenancing studies, a database of fully characterized Alpine copper mineralisations is being developed as the fundamental reference frame for metal extraction and diffusion in the past.

The abundances of about 60 minor and trace elements, including most transition metals and chalcophile elements, and Rare Earths Elements were measured in all samples via ICP-Q-MS. Furthermore, the feasibility of the routine reliable measurement of the $^{65}Cu/^{63}Cu$ isotope ratio [2] and its eventual use as a possible ore tracer was tested. Multicollector ICP-Mass Spectrometry was used to determine precise Pb isotopic ratios ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$).

Advanced strategies based on multivariate analysis were then used to discriminate the ore mineral provenance. Data were treated with the chemometric software "The Unscrambler Version 9.5" (CAMO AS, Trondheim, Norway). Data pre-treatment, PCA [3] and PLS-DA [4,5] models were performed as implemented in the software. Moreover, mines dataset was analyzed using inferential multivariate nonparametric methods [6,7].

Application of statistical analysis to the geochemical and isotopic database proved to be a very powerful tool to discriminate the ore source areas with very little ambiguity.

The applications to archaeometallurgical copper and slag specimens from the Agordo area (Veneto, Italy) and the recently found prehistoric slags from Millan (SüdTirol, Italy) indicate that the approach is successful in provenance and trade route investigations.

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Mineralogy of slags from South African prehistoric tin smelting activities

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A suite of vitreous slag remains from two prehistoric tin smelting sites at Rooiberg, Limpopo Province, South Africa were analyzed by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF), energy-dispersive X-ray spectroscopy (EDX), and electron microprobe analysis (EMPA). The cassiterite ore utilized at the Smelterskop site (ca. 1650-1850 cal CE) is associated with iron-rich tourmaline (schörl) and was mined from fracture fillings of rocks associated with the Precambrian granite intrusion of the Bushveld Magmatic Province. Evidence exists that the cassiterite feed was carefully beneficiated by panning of the crushed ore. Ore containing some zircon and rutile smelted at the Elandsberg Ledge site (15^{th}-17^{th} centuries cal CE) was presumably collected from alluvial placer deposits.

The mineralogical composition of the Smelterskop slags comprises skeletal cassiterite and complex spinels, as well as metallic tin prills ranging in size from a few to tens of micrometers. The spinels contain substantial amounts of tin, titanium and vanadium. The larger tin prills frequently contain Sn-Fe intermetallic compounds called 'hardhead' whereas the small, generally spherical blobs are essentially pure tin. Owing to the different composition of the ore feed processed at the Elandsberg Ledge site these slags contain in addition zirconium-rich minerals such as zirkelite, zirconolite and baddeleyite, and ilmenite.

In the presentation emphasis will be devoted to the role tin (II) and (IV) species appear to play during formation of the glassy slags as well as to the characterization of the complex spinels precipitated from the molten slag. From this study a consistent picture arises of the technology of prehistoric tin smelting in this part of the world.

Provenance determination of raw materials and production technology used in ancient mortars from Tournai (Belgium)

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At the Cathedral of Tournai in Belgium, archaeological excavations are exposing structures from Roman to Medieval age. Samples from these excavations have been subjected to a detailed investigation as part of a broader study considering the transition of ancient cities and their rural territories from Roman to late Roman society and the transformation to the early middle ages. Masonry mortars and mortars used for flooring have been characterized from the Imperial Roman period, the Carolingian style period and the Romanesque style period (4^{th} -11^{th} century AD) to trace the origin of the raw materials and to study the traditional knowledge on mortar production technology.

Computer assisted image analysis techniques were applied on thin sections of the mortar samples to obtain the grain size distribution curve of the aggregate [1]. The results were compared as a fingerprint with the grain size distribution curves of locally available sands, obtained with the same methodology. Based on the resemblance of the curves, it appears that locally available, fine glauconitic quartz sand was used integrally as an aggregate in some mortars, whereas it could not be excluded that somewhat finer sand, present in some mortar samples was sieved before use. However, no clear correlation could be established between the nature of the aggregate and the age or function of the mortar in which it was used.

To identify the origin of the binder a great number of binder related particles were investigated in detail using SEM/EDX and microprobe methods to investigate their nature. Three types of binder-related particles could be distinguished; underburned fragments, overburned fragments and lime lumps (sensu stricto). Underburned fragments as relicts of incompletely burned limestone helped to retrace its source, both Cretaceous marls/chalk and Carboniferous limestone have a highly variable Si- and Al-content and can therefore both yield a hydraulic or air-hardening lime. The presence of characteristic fossils and glauconite helped to refine the provenance of the chalk/marls used for the lime production. Overburnt particles gave helpful information about the burning and slaking of the lime. Overburnt particles containing wollastonite and rankinite associated with a C-S-H phase have been identified in several of the post-Palaeo-Christian mortars. These cathodoluminescent particles are scarcer in Roman and Palaeo-Christian mortars. They could be indicative for the selectivity of the ancient builders towards source materials and/or processed products.

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Fingerprinting of Cornish gold for provenancing prehistoric gold artefacts from Central Europe

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Previous studies of possible sources of gold used for the Bronze Age Sky Disc of Nebra initially pointed towards South Eastern Europe by indirect evidence, i.e. similar geochemical compositions of gold artefacts from this region [1]. The relatively high tin content in the gold of the Sky Disc, however, suggested a mineral association of gold and tin, similar to the one found in Cornwall. In this study, one lode and seven placer gold deposits from Cornwall have been analysed by LA-ICP-MS to determine the trace element signature of the natural gold for comparison with the gold inlays on the Sky Disc.

To characterise the locally heterogeneous composition of individual deposits as well as their nuggets, a minimum of ten nuggets per deposit as well as three points or lines per nugget were measured after pre-ablation had cleaned the surface. To compare the natural gold with the artefact gold, specific elements were selected, which, besides being useful for individual "fingerprinting", tend to show a low relative standard deviation (RSD) and a high stability during geological (fluvial transport) and metallurgical (smelting) processes. Mn, Co, Ni, Cu, Ru, Pd, Ag, Sn, Sb, Pt, Ir together with Au seem to be the most suitable elements, based upon the results of previous studies. The relatively strong natural variability of Au and Ag contents in natural gold, however, can result in a limited comparability with artefact gold. Artefact gold, on the other hand, can be alloyed with Cu, which is commonly geologically associated with elevated concentrations of Co, Ni, Ag, and Sb. The limited applicability of Ru and Ir for provenance studies is predominantly caused by their concentrations within natural gold being below the detection limits of the LA-ICP-MS instrument. The behaviour of elements that tend to partition into the slag during smelting, such as Mn, still needs further consideration. Since the geochemical signature of individual gold deposits gets homogenised during smelting, the mean value of each deposit has been calculated and used for correlation with the artefact gold.

For Cornwall, the trace element composition of the analysed natural gold strongly correlates with that of the gold inlays on the Sky Disk of Nebra. No similarly well matching "fingerprint" has been detected for previously studied gold deposits from Central and parts of South Eastern Europe. The best correlation is observed in the trace element pattern of the prehistorically important alluvial tin and (minor) gold deposit of the Carnon valley in South Cornwall, strongly suggesting this deposit as the source of the gold used for the Sky Disc. Recent studies of tin isotopes [2] suggest that the tin for the bronze of the Sky Disc also originates from Cornwall supporting the presumed concept of trade of metals from the Atlantic region towards central Germany during the Bronze Age. Further investigations, however, will need to be carried out based on the results of this study and the initial indications for a South Eastern European source of the gold as some important prehistoric gold mining districts have not been studied yet within this context.

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Archaeological gold provenance studies based on SR-XRF and micro-PIXE analyses

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The territory of today Romania was one of Europe main gold-producing areas since the Antiquity, mostly due to the deposits from the "Golden Quadrilateral" in the Apuseni Mountains, and less to the Eastern and Southern Carpathians deposits. The goal of the study is to find out if so-called "Transylvanian gold", originated either in the Apuseni Mts. or/and in the Southern Carpathians was used to manufacture some archaeological objects i.e. the twelve Dacian gold bracelets (Fig. 1). For gold artifacts, trace elements such as Te, Sb, Hg, Pb, Cu, as well as Platinum Group Elements (PGE), Sn, Ta and Nb are more significant for provenance than the main components i.e. Au, Ag. On the other hand, Sb, Te and Pb are specific for the Apuseni Mts. gold, whereas the presence of Sn might be characteristic for the alluvial gold from the Southern and Eastern Carpathians. Each bracelet weights around 1 kg and consists of a thick gold rod, 6 to 8 times coiled in the shape of a spiral. The rods range from 2.30 to 2.80 m in length and end with palm leaf-like ornaments. The SR-XRF analyses (Berlin BESSY synchrotron) show various Au (78.2 to 92.9 wt.%), Ag (6.3 to 20.3 wt.%) and Cu (0.3 to 2.1 wt.%) content [1]. Sn, up to 0.15 wt.%, and traces of Sb were also detected.

The data obtained for archaeological artifacts were compared with analyses of 22 native "Transylvanian gold" samples. The latter were studied by means of both SR-XRF (Berlin BESSY synchrotron) and micro-PIXE (Paris AGLAE accelerator and Legnaro micro-beam) techniques. The results show high Ag (8 to 30 wt.%) and low Cu (0.2 to 1 wt.%) amounts in all studied samples. In particular, gold from Southern Carpathians placer deposits contains Sn (150-300 ppm) whereas gold from the Apuseni Neogene hydrothermal deposits (veins) have a highly variable content of Te (200-2000 ppm) and Sb (150-300 ppm).

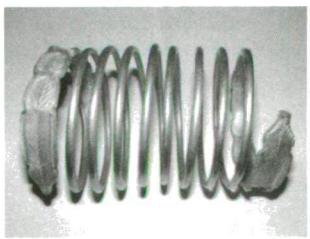

Fig. 1: One of the Dacian gold bracelets.

Due to the high possibility that the artifacts were manufactured from a mixture of native and previous gold object(s), it can be only presumed that at least partly, the metallic material used for the Dacian bracelets originated from the placer deposits from the Southern Carpathians and alluvial and Neogene veins from the Apuseni Mts. This is supported by the presence of Sn (for placers) and Sb (for veins).

Acknowledgements: Study supported by PN 91-020 project (Romanian Ministry of Education).

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Mineralogical and geochemical characterization of ceramic "sugar jars" ("formas de açúcar") from Aveiro town (Portugal)

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During the 15th to 19th centuries, the old pottery centre from the Aveiro town produced one typical form of ceramic called "formas de açúcar" ("sugar forms") or "cerâmica do açúcar" (Fig. 1), used only in the cycle of sugar production, specifically for the stage of the purge of the sugar cake. These ceramics were exported to sugar production areas, such as Madeira Island and Brazil.

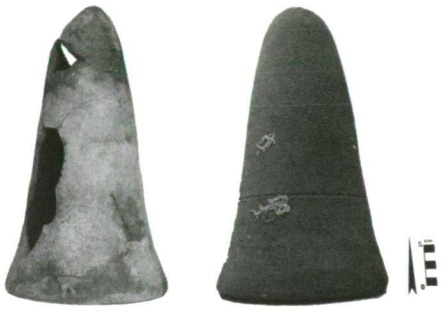

Fig. 1: Two ceramic "sugar jars" ("formas de açúcar") from Aveiro town (Portugal).

Such ceramics, including integrally preserved forms, were found at a sub aquatic archaeological site in a channel of Aveiro coastal lagoon. Same ceramics was found in the old urban areas, where mostly shards but also whole forms were used as construction materials for the walls.

In this work we present a synthesis of the main results obtained so far in the mineralogical and geochemical characterization of the ceramic "sugar forms" found in Aveiro (NW littoral region of Portugal).

Mineralogical analysis with X-ray diffraction was carried out on bulk samples, and on suspensions and oriented aggregates of <63 and <2 μm on air-dried, glycolated and heated samples. Scanning electron microscopy with elemental analyses was also done on selected samples. Chemical composition was assessed by X-Ray fluorescence and provided the major elements chemical data: SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MnO, CaO, MgO, K_2O, Na_2O, P_2O_5 and Loss-on-Ignition. Some trace elements such as: As, Sb, Cd, Co, Cu, Pb, Ni, Zn, Se, Te, Tl, and Ba were also analysed.

Multivariate statistical methods were applied, in particular, Cluster, Principal Components and Discriminant Analysis, the later being a statistical method that assigns samples to one or more of previously/-defined groups. The application of Discriminant Analysis, by means of the *Statistica* Software Program, implies that only the variables that exhibit variance in each defined group are used, leading to the exclusion of all others. The acceptation of both, the discriminant function and the variables that define it, is based on the interpretation of the Wilk's Lambda associated to each variable, and on the Classification Matrix. After verification of the validity of the determined function the Classification Matrix of each sample based on the posterior probabilities determined was interpreted.

The obtained results of composition have given important information about the provenance of the studied materials, and also about their raw materials. Mineralogical and chemical data obtained so far point to local production, using local and regional Upper Cretaceous (Maastrichtian) clays and sandy clays as main ceramic raw materials.

Prospecting for archaeological pottery provenance: experiences on Middle Neolithic Bükk culture pottery from Hungary

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Provenance investigations of archaeological pottery mean the tracking a complex manufacturing process which can involve both natural (sediments) and artificial (tempering) mixture of components. In addition, significant changes can affect the mineralogical and chemical composition turning from the raw material to the fired pottery (e.g. levigation of clay, tempering, firing, using, burial in sediment/soil). A possible and reasonable way of observation is to sample the possible raw materials and to compare them to the pottery. Investigation of silt-sand sized components (aplastics, temper) is based on petrography, but fine-grained constituents (clayish paste) require instrumental mineralogical and geochemical analysis.

Taking these aspects into consideration, our research group investigated Middle Neolithic Bükk culture pottery and natural samples of fine-grained soil-sediment profiles from different archaeological sites in Hungary (Aggtelek-Baradla cave, Bodrogkeresztúr, Felsővadász, Garadna, Boldogkőváralja, Sajószentpéter) [1,2]. Local sediments, mapped as Quaternary and Neogene in age, and partly soils were sampled by ca. 2 m deep hand drillings close to the archaeological sites. The samples were investigated as possible raw materials for pottery-making, shaped and fired accordingly. From the little "bricks", thin sections and powdered samples were made, same as for the archaeological pottery samples. Results of petrographic (PM), mineralogical (XRD) and geochemical (XRF) analyses were compared.

Based on our results, it can be stated that

(1) the near surface sediments/soils (similar to raw materials exploitable from shallow clay pits) can differ very much from the pottery found at the same site;
(2) in the 2 m lithological columns, there is large variety concerning mineralogical and chemical composition, which means that any similarity with the pottery material suggests intentional selection of raw material from the available local sources;
(3) mineralogical and geochemical data of pottery from various sites seem to cluster more tightly than that of the sediment/soil samples; even from one borehole;
(4) fabric and grains size properties suggest a definite physical quality requirement for the pottery raw material or specific treatment of that to reach the appropriate properties;
(5) fineware is even more consistent than average household ware;
(6) coarse household pottery shows more petrographic and geochemical affinity to the local soil samples than fineware.

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Written sources and archaeometric results: from fiction to truth

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Ancient and modern ceramic products can be studied from different perspectives. To the petrologist, they are artificial rocks which have been subjected to relatively high temperatures and have recrystallized to become thermometamorphic products, analogue to those naturally formed through metamorphism and anatexis. In contrast to natural rockforming processes, pressure is insignificant in the genesis of such objects, because the kiln can be considered as a technical system. In such open systems, neither pore solutions, present before firing, nor gaseous reaction products, which may have been produced during the high temperature process, have an influence on the transformation, because they can leave the system at any time. Similar to natural rocks, ceramic objects consist of an assemblage of crystalline and amorphic phases, which can be analysed with the same petrographic, mineralogical and chemical methods such as micaschists, which are formed from clay during metamorphism. Any ceramic fragment, how insignificant it may appear, can be compared to a potential 'book', because it contains, as if stored on pages, a wealth of information about its history. The lifespan of a piece of pottery can be divided into five steps: (1) extraction of the clay from the pit; (2) manufacture of the object (processing of the clay, firing); (3) use, with subsequent breakdown; (4) burial; (5) excavation, cleaning, treatment and analysis [1]. During all these steps, the sherd has stored information, and this 'memory' can be activated by a variety of chemical and physical methods [2,3]. Why study "young" ceramic objects, i.e. those from the 18th and 19th c. AD, when all aspects concerning the provenance and/or the specific technique are accessible in written, published or unpublished sources? Recent archaeometric projects showed contradicting results to the written convictions. Some of these studies of French and Swiss whiteware will illustrate the potential of mineralogical, petrographical and chemical methods in deciphering the real origin, the real recipe and the real technique of the studied objects. In all these cases, apparently firmly established written evidences are not reliable and must be revised.

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Characterization of the Copper Age ceramics of the Cucuteni-Tripolye culture (Ruginoasa site, NE Romania) by ICP-MS and EMP

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The Copper Age pottery exhumed at Ruginoasa, 60 km west of Iaşi (Romania) was assigned to the so-called Cucuteni-Tripolye cultural complex. It extended in the V-IV milenium BC from the central and north of today-Romania towards east, into Moldavia and Ukraine. Geologically, the region consists of Sarmatian clays, marls and sands, being part of the Eastern European Platform.

The elegant-shaped light red to orange pots, painted with white, red and brown-black geometric patterns are characteristic for this culture. Optical microscopy shows a red, porous ceramic body, with oriented texture. The matrix ranges from microcrystalline to amorphous. The non-plastic inclusions consist of quartz, plagioclase, K-feldspar, muscovite, biotite. Characteristic is the high number of fragments consisting of different clays and siltitic clays, partly calcareous. Other lithoclasts are scarce and consist of mainly metamorphics, some granite, grauwacke and silicastone. Granulometrically, the pottery classifies as fine ceramics, with maximum 3-4% arenitic grains.

The ceramics shows an intermediate to acidic chemistry, with 58.46-64.77 wt.% SiO_2, 12.78-16.64 wt.% Al_2O_3, 5.28-6.33 wt.% Fe_2O_3, 4.31-7.51 wt.% CaO and 2.73-3.48 wt.% K_2O. The content of Rb, Cs, Nb, Th, U and in particular Au (1.9 to 54.1 ppb) is relatively high.

The Backscattered Electron images revealed, besides the large non-plastic inclusions, a highly inhomogeneous matrix, consisting of a fine grained groundmass of clay minerals, amorphous phases and glass in which tiny, smaller than 0.02 mm non-plastic inclusions are embedded. The latter include quartz, feldspar, muscovite, some chlorite and calcite. Accessory minerals such as titanite, anatase, apatite, epidote and hematite occur as well.

Electron Microprobe analyses show that upon softening and possible partial melting the quartz grains, in particular along their rims, incorporate variable amounts of Al and K, with a trend in the direction of K-illite. The alkali-feldspar ranges from pure K-feldspar to anorthoclase and albite. Ca-bearing plagioclases are extremly rare. Muscovite varies from Al-rich compositions to phengitic micas with variable Fe and Mg content. They show a systematic decrease of Al and K and an increase of Mg, Fe and Ca. This transformation process of muscovite has a trend towards compounds with considerably less K and Al than usually measured in K-illite. The final firing products of clay minerals are crystalline, amorphous or glassy. Their composition resembles an intermediate compound between K-illite and a hypothetical Ca-illite with a wide range of composition. Such thermal transformations are obviously not unique in ceramics. They were also found in ceramics from Ilişua - a Bronze Age settlement in north Romania.

The non-stoichiometry of the newly-formed phases gives an insight into a fast firing, whereas their composition indicates a high temperature of firing, between 850 and 950°C.

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Mineralogical and geochemical „fingerprints" of historical bricks from Vienna

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Vienna has an at least 2000 years old tradition in making and use of bricks. The first bricks were probably produced by Romans in order to have enough construction material to fortify the Petronell and Vindobona military camps. We assume that the first brick-kilns were situated at the banks of the Alserbach River, where excellent raw material for bricks was available. During medieval times huge amounts of building material were needed to build and preserve the town walls. In particular, the urban expansion in the 19th century is a highlight in historical brick use.

Mineralogical and petrographical parameters as well as technological properties were analysed on several 100 to 300 years old brick (samples) from the surroundings of Vienna. In addition, elemental analyses were performed on total digestions of the powdered materials using inductively coupled plasma mass spectrometry (ICP-MS) as powerful technique for the determination of the trace element composition of the samples.

In the present work we aim to characterise which parameters are the most significant for tracing the origin of historical bricks. In archeometry it is a big task to determine the provenance and get information about the production technology in historical times.

Like in forensic studies, we are using an interdisciplinary approach to detect markers like „fingerprints" which are significant for the materials. The natural elemental distribution, characterised by the geochemical and geological environment and the technological process during the brick making, influences the chemical and mineralogical composition of the material. Additionally, different inclusions in the bricks like by-products or recycling material can be typical for different production places. Further to the variables measured, the signs – possibly the symbols of the producer – are available.

Several multivariate statistical methods like factor analysis, cluster analysis and discriminant analysis were performed on the data set. The available variables are manifold. There are more variables available than objects to be classified. It is therefore necessary to reduce the dimensionality and the multicolinearity. This is done with factor analysis. The factors are then used in the classification process. There are about 5 to 7 different sources and/or production sites for the 36 bricks. Discriminant analysis is used in two ways. One way takes the results of the cluster analysis as classes which are tested with the same variable set. Second the symbols on the upper side of the brick stones are used as different classes and the measured variables as explanatory variables to find out if the symbols could be used as hints about the different sources and production sites, which is obviously not the case.

Protohistoric amber in Europe: new data from Italy and state of the art

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The main European sources of amber are located in the Baltic region. Several Palaeolithic amber objects and the earliest workshop have been found in this area. In Southern Europe amber as workable material is employed much later, it appears in Italy in the Aeneolithic, and it is widely diffused in the Mediterranean word during the Bronze Age [1]. Amber deposits are also present elsewhere in Europe, but generally they supply a much smaller quantity of material with respect to the Baltic region, and the amber nodules are normally of limited size. The trade of Baltic amber is well documented during Roman times, whereas the hypothesis of Baltic amber diffusion throughout Europe since the Pre- and Proto-history has been long supported by archaeometric investigations [2,3].

The earlier archaeometric characterizations of the minor European amber deposits and of a few archaeological finds have not been followed by systematic investigations. Common knowledge that virtually all archaeological amber was imported from the Baltic regions has not been adequately supported or challenged by appropriate characterization of the materials, until very recent studies performed both on amber deposits and on archaeological objects. In some instances the use of local amber sources is proved since the Palaeolithic [4]. Our research is focused on the investigation of the amber sources of the earliest Italian materials, and on the change of sources and trade routes from the Aeneolithic to the beginning of the Iron Age [1,5].

The analyses have been carried out by infrared spectroscopy (FTIR), as a fast, inexpensive, poorly invasive and reliable technique for the characterization of amber [2,6,7]. The use of the Diffuse-Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) mode allows non invasive characterization or the use of a minimal amount of sample. About 200 objects have been analysed by DRIFT. The data show that succinite is indeed the principal amber type present in Italy during protohistory, though in a few sites the contemporary use of different amber sources is observed, especially in sites dated to the earliest Iron Age. As a matter of fact the archaeological objects found in two important Italian sites show the substantial presence of non Baltic amber [1,8].

The recent results on protohistoric Italian ambers will be presented and discussed as a function of material's age and geographic distribution, and compared to the available data on coeval European finds.

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Discrimination of prehistoric polished stone tools from Hungary by non-destructive chemical analyses

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Prehistoric polished stone tools with fine to very fine grained texture may show striking similarities in their macroscopic appearance by texture and colour. Therefore, it is very difficult to distinguish the different rock types by the naked eye. Prompt Gamma Activation Analysis (PGAA) is one of the powerful, absolutely non-destructive chemical methods for the analysis of archaeological materials. Contrary to other non-invasive chemical methods this technique measures bulk composition. As regards polished stone tools, PGAA measures all major elements and few trace elements [1].

189 polished stone tools from different collections and localities of Hungary, and 25 geological samples from potential raw material sources were analyzed by PGAA. To interpret the results, bivariant and ternary diagrams, as well as statistical analyses were used. To control the method, several broken pieces were studied also by destructive methods, mainly thin section petrography. Our aims were:

1) to obtain chemical composition of the analyzed artefacts;

2) to create an initial database of PGAA results of the most important raw materials of polished stone tools occurring in Hungary;

3) to explore the potentials and limitations of PGAA in the determination of the raw materials used for the polished stone tools.

As a result, several different raw material groups, basalt – dolerite – metadolerite, greenschist – metabasite – amphibolite, blueschist, hornfels, "white stone" (siliceous magnesite, siliceous siltstone, micritic limestone, tuff, diatomic schist) [2,3], ultrabasic rocks, acidic-intermediate volcanics, could be distinguished. Moreover, different rock types and their compositional varieties were recognized within each group (e.g. greenschist-metabasite, basalt-dolerite). It turned out that weathering or alteration can essentially change the chemical composition beyond the limit of recognisability of the rock.

Macroscopic description combined with PGAA will help to determine raw material types of polished stone tools. However, in some cases other methods are also necessary to achieve precise determination.

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Copper Age polished stone shaft-hole axes in Caput Adriae: archaeological implications

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During the Neolithic-Copper Age transition, production of polished stone axes in the Caput Adriae (northeastern Italy, central and western Slovenia and northwestern Croatia) underwent a drastic change in terms of raw materials and typology of the artefacts. Shaft-hole axes, mainly produced from meta-dolerites (A), serpentinites (B) and meta-ultramafites (C), became increasingly important in the Copper Age, spreading all over the region. However, the above mentioned rock types do not show a homogeneous distribution. Group A is concentrated in the southern part of Caput Adriae, group B in the northern one, and group C, not yet completely investigated, was unearthed mainly in the Karst and in central Slovenia.

Chemical, mineralogical and textural analyses, by Inductively Coupled Plasma-Mass Spectrometry, X Ray Diffraction, Electron Microprobe Analysis, Synchrotron Radiation Fourier Transform Infrared Spectroscopy, Optical Microscopy, were carried out. The results give evidence of a strong connection between provenance areas of the raw material and main copper mineralizations close to Caput Adriae. In particular, meta-dolerites come from Banija Ophiolite Complex at the northernmost edge of the Central Dinaric Ophiolitic Belt [1], while serpentinites probably originate in the Hohe Tauern area [2].

On the basis of these results, the position of Ljubljansko Barje (central Slovenia) - between eastern Alpine and Balkan copper-rich deposits - could contribute to explaining the importance of this area as metallurgical district at least from IV millennium BC, and, consequently, its important bridging role between Eastern Europe and the Mediterranean.

Finally, a possible source of raw material for the meta-ultramafites has not yet been recognized, even if preliminary indications suggest they could originate in Eastern Austria or Czech Republic.

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Archaeometric analysis on limnic quartzite-limnic opalite raw materials and chipped stone tools (Tokaj Mountains, NE-Hungary)

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Late-Badenian-Sarmatian siliceous sedimentary rocks from limnic basins of the Tokaj Mountains were commonly used for chipped stone tools in prehistory. These rocks have perfect physical and mechanical properties for this purpose. Due to the richness of the raw materials in several outcrops, they were accessible to the inhabitants of the area. Studying these tools helps to understand the history of the culture in this region. These facts demand a basic work to describe the outcrops, identify and characterise the siliceous rock types (generally with petrographic analysis).

The main goals of this study are comparing the limnic-quartzite, limnoopalite raw materials to chipped stone tools made from similar rock types, identifying the sources of the artifacts, extending the range of the technical methods and working out the methodology to identify the outcrops and quarries of the stone tools made of limnic quartzite or limnoopalite. To approach these goals, petrological, geochemical, mineralogical analysis of the artifacts and the possible raw materials were used and the results were compared. Detailed macroscopic and microscopic petrographic descriptions were made. XRF, NAA, PGAA were used as geochemical analysis and XRD, FTIR as mineralogical methods.

There is a clear relationship between raw materials and artifacts studied, according to the results of this study. A quarry could be assigned for most of the artifacts. The knowledge about the sorting method of raw materials for the stone tools was extended. Evidence for the suggestion of sorting parameters (phase/rate of silification, chalcedony content, opaline content) were found.

Petrographic and mineralogical methods were useful to identify the source of the stone tools in the Tokaj Mountains and to extend the technological knowledge (f.e. well thought selection of the raw materials). The geochemical methods should be useful for further exploration comparing more rock samples from the surrounding mountains (Matra Mt., Bükk Foreland, Börzsöny Mt. and Cserhát Mt.).

Different classes of matt-painted pottery from the sanctuary of the archaeological site of "Timpone della Motta" in the Sibaritide area (CS) Calabria – Southern Italy

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This study presents the comparison between three different classes of Matt-Painted pottery attributed to the 8th century BC from the sanctuary on the Timpone della Motta in the Sibaritide (CS), Calabria – Southern Italy.

Matt-Painted pottery was widely produced in southern Italy during the early Iron Age and finds from many indigenous sites underline that it was one of the favored pottery types both for dining and storage purposes. The term Matt-Painted refers to handmade vessel of typical indigenous shape with applied decoration in a matt dark paint.

Traditional archaeological research divides Matt-painted pottery into a range of regional classes based on the decorative styles of each region. The thousands of fragments from the sanctuary on the Timpone della Motta, together with the finds of Matt-Painted vessels in indigenous graves and houses, show that two predominant styles were present in the Sibaritide. These two styles have been named the "Undulating Band Style" and the "Fringe Style" based on their many decorative elements. In addition, another range of stylistic groups may be observed in the local indigenous pottery production. Recent research has, however, documented a group of Matt-Painted pottery on the Timpone della Motta, which is notably different from all other Matt-Painted vessels on the site. These vessels display a high level of craftsmanship in being very thin-walled and decorated in a miniaturist and very elaborated style. The closest typological and stylistic ceramics are found among the Matt-Painted pottery productions in the southern Salento region, which naturally raises the question if the vessels from the Timpone della Motta were imported from the Salentine area. In that case the fragments from the Timpone della Motta constitute the only example of deliberated export of Salento Matt-Painted pottery.

Twenty nine fragments of Matt-Painted pottery (one sample was misfired) have been submitted to petrographical analysis applying optical microscopye, mineralogical XRD analysis and chemical analysis in XRF with the aim to investigate on different ceramic productions. The results show that the composition of the "Undulating Band Style" and "Fringe Style" fragments is analogous, while is different the composition of the six ceramic fragments with characteristics similar to the Matt-Painted potteries of the southern Salento region.

Another important aim is to clarify possible correspondence between the used raw material and local clay deposits. For this purpose the clay sediments collected around the archaeological site have been submitted to mineralogical analysis in XRD, chemical analysis in XRF and granulometric analysis. The SEM morphological study of the fragments is devoted to the distinction between different workshop techniques.

Analysis of bricks from Brazilian historic places

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This contribution presents results of the qualitative determination of the chemical elements in Brazilian and Dutch bricks found in historic places in the State of Pernambuco, located in the Northeastern Region of Brazil. Seven bricks, two dated in the 17th century (Dutch bricks), one from the 18th century, three from the 19th century, and one from the 20th century, were analyzed by means of energy dispersive X-ray fluorescence (EDXRF) and X-ray powder diffraction (XRD) in order to identify the mineral phases. The XRD results are displayed in Table 1.

Table 1: Mineral phases identified in the brick samples by XRD

Red-brick (Dutch)	Yellow-brick (Dutch)	Building "Convento de Santo Antônio"	Building "Casa de Câmara e Cadeia"	Building "Casa de Câmara e Cadeia" Nº 03
(17th century)	(17th century)	(18th century)	(19th century)	(20th century)
Quartz	Quartz	Quartz	Quartz	Quartz
Kaolinite	Kaolinite	Illite	*	Illite
	Anorthite	Anorthite		Rutile

*evidence of kaolinite with low crystallinity.

To identify possible patterns in the data, the Principal Component (PC) analysis was applied. For each brick, four points were measured by EDXRF. The results illustrate the differences in the composition among the samples, and allow a Fe and Ca based discrimination. Five distinct clusters resulted and they reflect the inter-correlation or covariance degree among few of the principal components, as shown in Fig. 1.

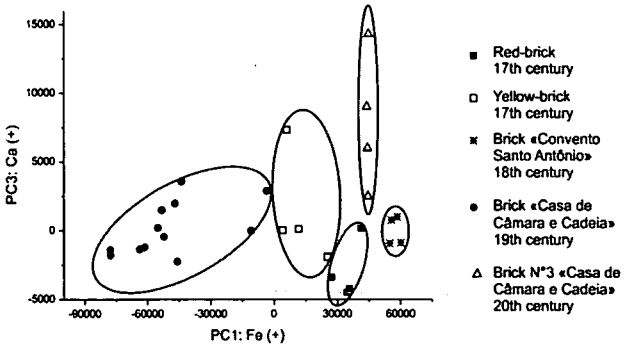

Fig. 1: Principal component analysis based on EDXRF data: PC1: Fe(+) (positive influence) versus PC3 Ca(+) (positive influence).

These results indicate that the bricks were manufactured from different raw materials, i.e. clays, in different times and places.

Microstructure and composition of glaze of Haban ceramics from Sárospatak (NE-Hungary)

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Production of tin-glazed ceramics (faience) in Central Europe, thus in the historical Hungary as well, was established by Haban (Anabaptist) potters. In the 16th century Anabaptist ceramists had to emigrate from Switzerland, South Germany and Italy due to religious repression, and they moved to Austria, Moravia and Hungary and in the 17th century to Transylvania and further. They brought their skills and implanted a local pottery production under the influence of their new artistic language.

Notable settlement of Habans in Hungary occurred after 1620. In 1645 one of their groups moved from Moravia to Sárospatak (NE-Hungary) where they lived until 1680. One of the main activities of the settled Habans in Sárospatak was pottery, among others faience production.

Archaeological excavations in the last years revealed a 17th century cannon and bell casting workshop in the yard of the Sárospatak castle. During the excavations fragments of tin-glazed ceramics were found, which were most probably produced by the local Haban workshop.

There are no written sources from the 17th to 18th centuries about the production technology of Haban (tin-glazed) ceramics. Our archaeometric research focuses on the mineralogical, petrographic and geochemical investigation of the ceramic body, the white, tin-opacified glaze and the decorations of different colours, and aims to identify the used raw materials and to reconstruct the production technology.

Preliminary electron microprobe analyses indicate that white glaze of the Sárospatak faiences is lead-alkali type with ~38 wt% PbO, 2.2 to 4.4 wt% SnO_2 and 4.9 to 5.8 wt% K_2O+Na_2O content (according to EDS spot analyses). The opaque glaze layer contains tin oxide particles and aggregates (SnO_2 is present in orthorhombic and tetragonal forms according to X-ray diffraction analysis), and relict grains with Sn-Pb-Si composition. Rounded to subangular quartz and feldspar particles are also present.

Decorations were made by using coloured (yellow, blue, green and black) glazes. Blue decoration is associated with cobalt (0.7 to 1.4 wt% CoO) and contains significant amounts of arsenic, nickel and iron as well (1.6 to 2.1 wt% As_2O_3, up to 1.3 wt% NiO, 1.3 to 1.8 wt% FeO) suggesting use of impure cobalt ore (zaffre). Yellow decoration contains lead antimonite particles ($Pb_2Sb_2O_7$ according to X-ray diffraction analysis) and significant amount of dissolved iron (>3 wt% FeO) is also present in the matrix. Black decoration was prepared by using manganese colorant (>2.5 wt% MnO).

A metabasite shaft-hole axe from Grotta Azzurra di Samatorza (Trieste Karst): first evidence of connections between northeastern Italy and central Europe during Neolithic

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A fragment of a shaft-hole axe, made from a metabasitic rock, was found in the second half of last century in the Grotta Azzurra di Samatorza in Trieste Karst (northeastern Italy). The artefact, without stratigraphic information, was previously attributed to a general Dinaric origin.

Recently, thanks to the systematic interdisciplinary study of polished stone axes from Caput Adriae (northeastern Italy, central and western Slovenia and northwestern Croatia) [1;2], it has been discovered that the artefact is texturally and mineralogically indistinguishable from the Jizera Mts. fine-grained amphibole-rich metabasites [3]. These rocks belong to Krkonoše-Jizera Crystalline Unit (Bohemian Massif).

This material has been largely employed for the production of polished stone axes during the Neolithic of central Europe [3]. The distribution of the Jizera Mts. raw material includes a wide area - Bohemia, Moravia, western Slovakia, southern Poland, Germany and probably northern Austria and Netherlands.

According to the available data the axe from Grotta Azzurra is the southernmost ever found. It is a rare archaeological proof of early connections between Caput Adriae and central Europe (whose directions still have to be fully understood). This is also testified by a few occurrences of Carpathian obsidians in the Danilo/Vlaška archaeological sites of Caput Adriae.

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Analysis of some ancient Roman mortars from Ulpia Traiana Sarmizegetusa (Romania)

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Ulpia Traiana Sarmizegetusa was the capital of the Roman province Dacia. The city was founded by the emperor Trajan in the early 2nd century AD, and deserted in 271-274 AD under the rule of emperor Aurelian. At its maximum development, it had over 20,000 inhabitants.

This study focuses on several samples of mortars from different walls and structures (probably a bone-processing workshop, the prison, the pedestal of Trajan's statue and the school of gladiators). In the case of the samples from the recently unearthed bone-processing workshop larger samples of mortar from the walls were collected (up to 7 cm in thickness), where we could observe different layers meant to level the surface of the walls, from the other locations smaller pieces from the outer parts of the walls were selected.

The collected samples were studied by optical microscopy (thin sections), XRD and thermogravimetry.

The mortars have a porphyroclastic texture and in general the aggregate includes 1 to 5 mm-sized lithoclasts, crystalloclasts and ceramoclasts. One notable exception is represented by the mortar from the thick walls of the workshop which additionally contains fragments of ceramics in the centimetric range (up to 3.5 cm in length). The crystalloclasts are mainly represented by calcite, quartz, plagioclase and K-feldspars, muscovite, epidote, magnesiohornblende and pyroxene. Quartz clasts fissured due to thermal shock were identified in some thin sections. Feldspars are frequently transformed into clay minerals and sericite. The whole matrix is carbonatic, with secondary calcite deposited in pores and fissures. The lithic fragments consist of quartzites, micaschists, gneisses and limestones. In one thin section fossil remains could be observed. Two samples contain visible straw and plant remnants.

The ratio between CO_2 and the structurally bound water from the thermogravimetric data suggests that some mortars were of hydraulic type. Others were probably of subhydraulic type: lime was obtained from a purer limestone and therefore the mortar did not yield a hydraulic binder.

According to the identified mineralogical composition we presume that the raw material which was used has a local provenience. The metamorphic material used as aggregate comes from the nearby Retezat Mountains (Southern Carpathians), and is common in the alluvia of small rivers. It was probably extracted from pits. Limestones were most likely quarried 5 km west of the city.

Mineralogical and chemical study of ceramic sherds and clay samples from Cameroon

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This work is a contribution to the archaeometry of ceramics from Cameroon. Ceramic sample material together with regional clay material were collected in three regions of Cameroon: Mfomakap-(Central region), Mombal-(Eastern region), and Zamala-(Far North region). The purpose of this work is to find answers to the questions of the provenance of the ceramics (local production, imported ware?) and the production techniques (processing of raw material, moulding of vessels, firing temperature and conditions).

The polarized light microscopy, X-ray diffraction, X-ray fluorescence spectrometry, differential thermal analysis, thermogravimetry, and X-ray computer tomography were used as analytical methods.

The results of thin section analyses show that quartz is always the most abundant component (70-80%) of the temper. Additional minerals are micas, mainly biotite, scarce K-feldspars and very rare plagioclase in Mombal, plagioclase, some K-feldspars and rare biotite in Zamala, hornblende, K-feldspars, biotite and plagioclase in Mfomakap. These mineral combinations suggest that the potter's workshops were situated in a landscape with more or less acidic magmatic rocks.

The mica-flakes and the arrangement and shape of pores in the sherds from the three regions do not show any preferred orientation, as one would expect if the objects had been shaped by means of a potter's wheel. All the ceramic artefacts were probably hand moulded.

The X-ray diffraction analyses of sherds show the presence of quartz, K-feldspars and biotite in all three areas. Additionally, kaolinite is observed in Mombal, hornblende and plagioclase in Mfomakap, and plagioclase in Zamala.

According to the results of X-ray fluorescence analyses of ceramics and raw material, local clay as it comes from the pit was used for making the pottery in Mombal and Zamala. In the case of sherds from Mfomakap the chemical data suggests that the raw material was obtained by mixing two types of clay, one rich in Al_2O_3 and rather low in SiO_2 and the other rich in SiO_2 and rather low in Al_2O_3.

Firing experiments in conjunction with DTA/TG and X-ray diffraction analyses with clays from the three locations showed that kaolinite disappears through an endothermic reaction between 400 and 500°C (onset temperature 470°C), illite breaks down between 900 and 1000°C, and mullite forms in the range of 1000 – 1100°C. Comparing the phase assemblages of the sherds with the phase assemblages of fired clay samples, the firing temperatures were deduced.

In conclusion, the pottery of the three regions seems to be a local production. The firing temperature was always below 900°C. In Mombal the presence of kaolinite in the ceramics indicates a firing temperature below 500°C. In sherds from Mfomakap and Zamala micas are still present and this finding points out to firing temperatures below 900 - 950°C.

Archaeometric study of the Neolithic pottery from the "Le Grottelline" site (Spinazzola, Italy)

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The archaeological site of "Le Grottelline", in the territory of Spinazzola, province of Bari (Southern Italy), dates back to the ancient Neolithic Age. Abundant ceramic materials were recovered, which mainly belong to the Culture of "Archaic-Impressed Pottery" and appear similar to those found in other Neolithic sites of the area [1].

The archaeologists recognised four ceramic classes: coarse, semi-depurated, depurated and *figulina*, even though in many cases it was difficult to make a clear distinction between them. In fact, coarse and semi-depurated ceramics differ between them only for the dimensions of the inclusions, while depurated ceramics differ from *figulina* mainly due to its macro-porosity. Semi-depurated and coarse ceramics represent the main part of the recovered pottery (about 80%).

Three samples were selected for each of the four classes for the archaeometric investigation, which was carried out mainly by means of optical microscopy in thin section, WDS-X-ray fluorescence, and X-ray diffractometry.

The results individuate two ceramic classes: coarse pottery and fine pottery, and three isolated samples. Coarse pottery is constituted by large silicate inclusions in a fine carbonate-poor clay matrix and includes samples from the archaeological coarse and semi-depurated classes. Fine pottery includes the *figulina* ceramics, together with one 'depurated' sample and one semi-depurated sample, and is characterised by medium calcium contents (10-13% wt CaO). The three isolated samples differ from the previous ones both for the microstructure and the chemical composition. The crystalline phases allow to hypothesize a firing temperature <800°C for the coarse pottery and the isolated samples, and 800 to 900°C for the fine pottery.

Comparing our archaeometric results with those of other Apulian Neolithic sites, great similarities have been registered in particular with pottery from Pulo di Molfetta, considered as local production [2]. On this base, also the main part of the "Le Grottelline" pottery has to be considered as local. In addition, the raw materials show geological features typical of the Murge Plateau that is characterized by the presence of calcareous-arenaceous-argillaceous deposits with frequent fossiliferous levels and shaley marl horizons are present.

The variations in the microstructural and chemical characteristics could be attributed to different collecting areas and/or to the nearness to the Bradanic Hole, in which fine quartz-rich micaceous sands are present.

On the base of all the obtained results, the pottery of "Le Grottelline" site shows the technological characteristics of the Ancient Neolithic productions, that used raw materials not so far from the housing areas, often without purification. The firing process was carried out by means of systems with low-medium temperatures and prevalently oxidant firing atmosphere, even if fluctuations were possible, which are responsible of the chromatic variations of the pieces.

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The browning phenomenon of medieval stained glass windows

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Manganese is a chemical element which has long been used as a colouring or a bleaching ingredient in the glass industry. Its existence at various oxidation states is at the origin of a large variety of colours. This latter can evolve according to environmental parameters such as radiations or the atmospheric pollution. In some ancient stained glass windows, the simultaneous presence of manganese and iron, coupled with the alteration by water and micro-organisms, can induce a browning and, consequently, a loss of transparency in stained glass windows.

To better understand this browning phenomenon, ancient stained glass windows displaying a browning are characterized using optical microscopy, SEM-EDS, microprobe analysis and XAS at the Fe *K*-edge. The ancient glasses that present the browning phenomena appear to be potassic glasses and more precisely calco-potassic samples that contain equivalent quantities of CaO and K_2O. In these potassic glasses, the brown zones are very rich in Mn as compared to the fresh glass but also to the altered glass. In parallel, the Mn-oxidizing bacteria (*Burkolderia Cepacia* [1]) present on the historical samples are isolated and cultivated. Finally, simplified model glasses of various compositions but containing the Fe/Mn couple will be altered in presence of these microorganisms.

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A petrographical study of lithic tools from Petreşti archaeological site (Romania)

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The present study focuses on ten lithic tools recovered from Petreşti archaeological site, located 4 km south of Sebeş (Southern Carpathians), now in custody of Sebeş Town Museum. The objects belong to the Petreşti Neolithic culture, dated between 2400–2100 B.C. [1] and famous mainly for its painted ceramics. The objects were submitted for a mineralogical-petrographical study, in order to establish the rock types and, furthermore, to identify possible source areas for the raw materials.

Based on the definition of typical functional Neolithic tools (i.e. simple axes, truncheons, fighting axes and hammers [2]), nine samples classify as axe-hammers (according to the criteria defined by Iuliu [3]), and one is a truncheon with three bumps. For the truncheon-shaped one, a decorative purpose is presumed. In order to determine the shape, size and colour of the objects, macroscopical investigations with the naked eye or with a magnifier were carried out. The tools are made of rocks with relatively high hardness. They are very well polished and all but one have similar shape. Predominantly their colours are dark (grey, brown, black), but in three cases lighter hues were observed.

For the optical microscopy investigation, small fragments of the lithic objects were sampled by wet coring with an electrical drill (10 mm in diameter) to a maximum depth of 15 mm, and prepared as thin sections. Mineralogical and petrographical (structure and texture) features were observed by using a Nikon Eclipse E200 Pol microscope with an attached digital camera. A dominant microgranular massive texture was revealed, with local porphyric varieties. One sample has orientated texture. All the three main genetic rock types were used as raw materials (in brackets, number of tools within the group): igneous (diorite, andesite with hornblende and basaltic andesite) (3), metamorphic (sericite-chlorite schist, metapsammite, serpentinite, hornfels with quartz) (5), and sedimentary (chemical precipitation limestone, sandstone with quartz and feldspar) (2).

In order to identify possible sources of raw materials for the investigated lithic objects, the geological structure of the area was studied. According to the geological map, Orăştie sheet (1:200.000), not all the rock types identified as raw materials in this study can be found around Petreşti village. The area is mostly covered with Holocene sediments. Therefore, knowing the petrographic nature of the ten tools, it can only be concluded that most of the raw material (metamorphic and sedimentary rocks) was either transported by Sebeş River, which springs in the Southern Carpathians. Regarding the provenance of the igneous rocks, they could come from the Mureş River alluvia. This river collects similar rocks from the Apuseni Mts. The exact structural units delivering all raw materials have to be further investigated.

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Provenance of graphite in Celtic graphitic ceramics from North-west Romania

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The Celts settled in the Carpathian basin in the 4th century B.C. (Iron Age, La Tène period) from Western Europe. Their expansion took place in two main directions leading to two significant settlement areas: the Transdanubian region, along the Danube towards Serbia as well as the Hungarian Northern Mountains, the North-west Romania and the southern territories [1].

Peculiarity of the Celts was the production of graphitic (i.e. graphite-bearing) situla-type ceramics. Graphitic ceramics are found not only in the close vicinity of the geological occurrences of graphitic rocks, but also on archaeological sites scattered all around Europe, which suggests an extensive trade of graphitic ware or graphitic raw material. Former archaeometric studies [2,3], carried out on Celtic graphitic ceramics from the Transdanubian region, indicated that graphitic rock temper was probably originated from the South Bohemian Massif (from the Variegated unit in the Southern Czech Republic).

The present archaeometric study focuses on graphitic ceramics from several archaeological sites of North-west Romania [4,5] to determine the source (provenance) of the graphitic temper. Vessels investigated derive from 9 localities: Érendréd / Andrid (1), Kálmánd / Căminl (2), Börvely / Berveni (3), Piskolt-Kincsverem / Pişcolt-Lutărie (4), Mezőfény / Foieni (5), Bere-Nyúlvár / Berea-Nyúlvár (6), Piskolt-Gárdovány / Pişcolt-Gárdovány (7), Nagykároly-Bobáld / Carei-Bobald (8) and Lázári / Lazuri (9) (Fig. 1).

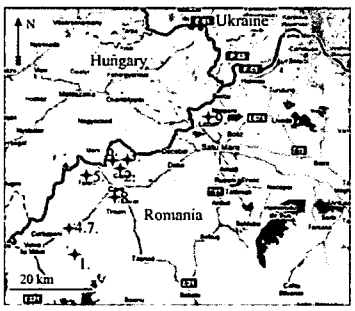

Fig. 1: Location of the archaeological sites of the studied graphitic ceramics in North-west Romania.

Graphitic rock fragments found in the studied north-west Romanian ceramics consist of graphite, quartz, K-feldspar, plagioclase, kyanite, sillimanite and altered mica. The graphitic rock used as temper for ceramics is medium to high grade metamorphic rock, graphitic paragneiss. Formerly studied graphitic ceramics from the Transdanubian region show similar mineralogical composition [2,3].

Based on metamorphic grade and mineralogical composition, the potential provenance of the graphitic rock fragments is the Variegated Unit in the Moldanubian zone of the Bohemian Massif. Celts in North-west Romania used the same trade network for importation of graphite (graphitic rock) or graphitic ceramics as the Transdanubian population.

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Provenance and technology study on a collection of loose garnets from a late 5th century Gepidic grave in Northeast Hungary

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Red gemstones identified mostly as garnets generally occurred in the 5th-6th century Europe as decoration of fine metal works. They are known mainly in mounted form, the loose, unmounted pieces are very rarely found. Therefore, it is of great importance that seventeen such loose red gemstones were unearthed at a rescue excavation at Hajdúnánás-Fürj-Halom-dűlő (Hajdú-Bihar County) in a late 5th century cemetery of the Gepids, an East Germanic tribe settled on the eastern bank of the Tisza River from the late 4th century. The discussed pieces considered as remains in a robbed grave were investigated in order to identify the mineral species, its provenance and the technology of cutting. The lack of any related goldsmith's artefact and the visible different phases of the gem-cutting process allow us to regard them as independent pieces of a collection. The noticed inclusions and the measured refractive index revealed that the discussed gemstones are garnets. In addition to the gemmological observation, the analysis was focussed on the chemical composition. The resulting spectra were obtained by a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) and display characteristics of Fe-rich as well as Fe-Mg-rich garnets, i.e. *almandine* and *rhodolite*. The comparison of the concentration ratios of the major constituents with the literature data suggests that while the almandine garnets may have been imported from Rajasthan, North India, the rhodolite garnets may have been mined in Sri Lanka [1]. The image analysis based on optical and scanning electron microscopy clearly showed traces left by polishing and shaping. All of the six flat cabochons and seven of the flat plates look like semi-finished products where final steps of shaping were not carried out. Besides, the other four plates may be regarded as finished products with regular shapes. In some cases intentionally engraved outlines were noticed running along the edges. These straight shallow grooves were interpreted as an indirect proof for the use of a template or a sort of pointed marker. Based on our observations, the cutting process could be reconstructed, and the following steps were inferred: 1) cutting the raw surfaces to the desired steepness and thickness; 2) polishing these surfaces on the top and base; 3) designing the shape and size of the prepared pieces by a marker (occasionally) and finally 4) cutting off or breaking the unnecessary edges. Considering the semi-finished pieces characterized by irregular edges, the final steps of their shaping were apparently carried out in a satellite or local workshop. This observation contributes to the recurring debate about the character of imported garnets [2]. The discussed findings suggest that in the Early Middle Ages garnets for inlays were traded in the Carpathian Basin both in pre-cut and ready-to-set form. While mounts and cell walls usually make the accurate observation difficult, the loose character of these pieces permitted us to perform an extensive investigation focussing both on the raw material and the technology. Results may clarify or identify the geographical origin as well as the applied equipment and the organisational aspects of gem-cutting.

Acknowledgements: The study was carried out with the support of the Archaeological Research Laboratory, Stockholm University, Sweden. Help of Brigit Arrhenius and Maria Wojnar-Johansson related to this research is highly appreciated.

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Mineralogy and geochemistry of Bronze Age potsherds: weathering influence of a Mediterranean climate (Cres Island, Croatia)

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The aim of this study was to study the causes of well preserved status of potsherds in Bronze Age hill forts on Cres island (Northern Adriatic Sea) exposed to Mediterranean climate and their buried equivalents in colluvial deposits. The island of Cres has a long history of settlement and hosts some very important Mesolithic, Neolithic and Bronze Age sites. Due to erosion large areas are bare karst lacking soil cover and prehistoric potsherds can be found in stonewalls of hill forts or caves.

The potsherds were analyzed by microscopy methods as well as geochemistry to study the weathering process in both exposed and buried potsherds. The colluvial soil containing potsherds was dated and a calibrated ^{14}C AMS date ranging from 2030 to 1870 BC was obtained. Under the optical microscope, the potsherds are texturally homogeneous and display inclusions of similar type, abundance, and grain size. XRD analyses show that they contain quartz and calcite as dominant mineral phases, and fewer amounts of micas and feldspars (K-feldspar and plagioclase).

The enrichment of Ca in exposed potsherd rims is accompanied by depletion of light REE's and enrichment of heavy REE's. The results show that potsherds exposed to the Mediterranean climate for four thousand years have an improved durability due to calcite re-crystallization and notable change in the chemical composition of potsherd rims which have to be considered when using bulk geochemistry for provenance studies.

Mineralogical investigations of clay-bricks from Árpád-age (11th-14th century A.D.), southern Hungary

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During the so-called "Árpád age" (11th-14th century A.D.) clay-bricks were a common building material in the southern region of The Great Hungarian Plain (Szeged-Békéscsaba region). In the area, it was mainly the local production that provided bricks for churches and monasteries.

Brick samples from nine archaeological sites (churches and monasteries from the Great Hungarian Plain), now in the custody of "Munkácsy Mihály" Museum of Békéscsaba, were selected for the study. Representative specimens were obtained by sectioning and weight reduction of samples. Optical and Scanning Electron Microscopy, Electron Microprobe and X-Ray Powder Diffraction (XRPD) investigations were used to determine the mineralogical composition of samples, and to constrain the firing temperature.

Although the archaeological sites are closely located, for the purpose of comparison between different groups of sites, the samples were separated in four groups: I. Örménykút (Ö)-Décse (D), II. Kamuth (K)-Megyer (Me)-Gerla (Ge), III. Gyula (Gy) and IV. Bánkút (B).

The mineralogical composition of all brick samples is highly similar and points to illitic clays. The abundant use of vegetal tempering materials (wheat chaff) in most of the studied bricks is characteristic. The presence of dolomite is only observed in one of the Örménykút samples.

Several neoformation phases due to firing, such as K-feldspars (anorthoclase–sanidine), anorthite, gehlenite, diopside were detected (Fig. 1).

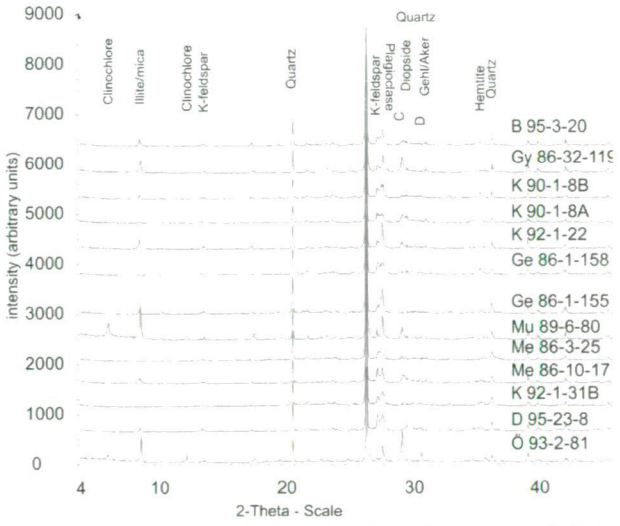

Fig. 1: XRPD diagrams of the investigated samples (Cu-Kα radiation).

The mineralogical composition of primary components, as well as the newly-formed phases upon firing, suggests the use of similar raw materials, i.e. Ca-rich illitic clays.

The type and amount of firing phases indicate temperatures in a range of 900-950°C. Only one sample from the group II shows a lower firing temperature, around 850°C.

The mechanism of thermal decomposition of dolomite and its implications in pyrotechnology: new insights from 2D-XRD and TEM analyses

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Dolomite has been thoroughly used for ceramic and building purposes (e.g., dolomitic lime mortars) since ancient times. Pyrotechnology of dolomite ($CaMg(CO_3)_2$) involves its thermal decomposition into CaO and MgO. This process, called calcination, influences the physicochemical properties of dolomitic limes and affects the textural properties of dolomite-based ceramic materials. Although the thermal decomposition of dolomite has been studied for more than one century, the mechanisms of this reaction still remain obscure.

Here, single crystals of dolomite were calcined in air atmosphere at a T range of 500°C-1100°C, and analyzed by XRD, 2D-XRD, FESEM and TEM. Decomposition was also studied in-situ, by the TEM, by irradiating dolomite crystals with the electron beam. The decomposition is pseudomorphic and topotactic, and results in oriented CaO and MgO ((Ca,Mg)O) nanocrystals, which aggregate and grow as T increases. In-situ TEM shows that the first step of decomposition involves the formation of a face centred cubic (Mg,Ca)O mixed oxide, with the following orientation relationships: $[-441]_{dolomite}//[001]_{oxide}$ and $(110)_{dolomite}//(110)_{oxide}$ (Fig. 1). 2D-XRD results are consistent with in-situ TEM results, and show the presence of highly oriented oxides in the dolomite pseudomorph. Unlike the case of the in-situ TEM decomposition, the range of (Ca,Mg)O solid solution is very limited (up to 8%) and only occurs at low T (500°C – 750°C). A further T increase leads to the formation of oriented, pure CaO and MgO nanocrystals. In air, thermally activated ion diffusion favours de-mixing (spinodal decomposition) of the initial (Ca,Mg)O phase as T increases. Conversely, "cold" in-situ TEM decomposition prevents de-mixing of the initial (Ca,Mg)O.

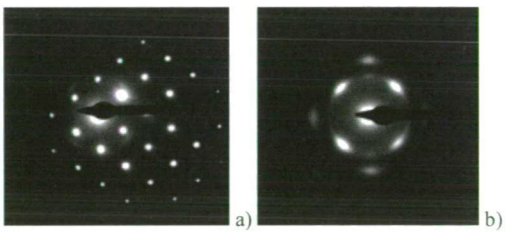

Fig 1: Selected area electron diffraction (SAED) images before decomposition of (a) dolomite ([-441] zone axis), and after its decomposition into (b) a mixed Ca-Mg oxide ([001] zone axis).

These results show that the thermal decomposition of dolomite involves its direct transformation into a mixed Ca and Mg oxide (at low T), and subsequent separation into two oxides (spinodal demixing) with increasing T. The reaction is topotactic and independent of pCO_2. Formation of $CaCO_3$ during the so called "half decomposition" of dolomite was observed in some runs. However, either calcite or vaterite formed. The fact that vaterite has no structural relationship with dolomite suggests that previous models based on the transformation of dolomite into $CaCO_3$ plus MgO (i.e., "half decomposition" of dolomite) are flawed. Apparently, $CaCO_3$ formed during re-carbonation of highly reactive CaO nanocrystals. This solves the problem of the so-called "two-stage" decomposition of dolomite. These results may help in constraining processing parameters (e.g., calcination T) in ancient dolomite-based ceramics, and may also help defining appropriate processing parameters during preparation of modern dolomitic lime-based conservation mortars.

The raw materials and manufacture of pottery during Bronze Age-Early Iron Age in the North-Western Russia

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The ceramic artifacts are the main material which can be used for reconstruction of prehistoric people life and different cultural traditions. Numerous settlements of Bronze Age – Early Iron age (2000 cal. BC – 500 cal. AD) were excavated in the area of basin of Volkhov River basin (Shkurina Gorka, Porogi sites:800cal BC-400 cal.BC, Kholopii Gorodok site: 800cal.BC-500cal AD); Ilmen Lake (Prost' site: 800calBC-400 cal.AD, Gorodok na Lovati site: 10cal.AD-500cal.AD, Sel'tco site: 800calBC-400cal. AD); Ladoga Lake (Ust'-Ribezgna II site: 2000cal.BC-1500cal.BC), located in the North-Western Russia. It is one of the perspective regions of archaeological works on the North-Western of Russia in the present time. The main problem is the chronology and cultural attribute of different sites and their connection with sources of raw materials.

The investigation of pottery included a complex approach. To determine the cultural and historical belonging of ceramics the archaeological methods (typology and morphology) were applied. The mineralogical and geochemical methods (optical microscopy, XRD, thermal analysis, XRF) were used for the determination of the ceramic composition, the manufacturing technology and the sources of row material (more than 70 samples of ceramic sherds and 16 samples of clay raw material).

Based on both the mineralogical composition and geochemistry of ceramic material and the archaeological typology, a number of ceramic type groups were distinguished. The ceramics of Bronze Age (Ust'Ribegna II site) consist of montmorillonite clay and disintegrated plant remains; the estimated firing temperature was about 650°C. The ceramics of Volkhov type (Shkurina Gorka, Porogi, Prost', Kholopii Gorodok, Sel'tco sites) consist of kaolinite-illite clay, crushed gravel of granite-plagioclase composition and grog; the estimated firing temperature was around 500-700°C. The Iron Age ceramics (Kholopii Gorodok, Gorodok na Lovati sites) consist of illite clay and a temper made of crushed granite-plagiogranite gravel; a firing temperature around 800°C could be infered. These characteristics give possibilities for identification the ceramics from different settlements and chronological periods.

The changes of environmental conditions about 1500 cal. BC (Ladoga Lake transgression) most likely influenced the prehistoric people life. The flood on Ust'Ribegna II site was one of the reasons of that the population has left this place and changes the raw material sources for pottery produced in this and successive periods.

Characterization of earthen building materials from a Phoenician site, Malaga (Spain)

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Earthen building materials, adobe walls and pavements, were characterized to determine the materials composition and constructive techniques from a Phoenician site. Clay samples from the surroundings were also studied, to identify the raw materials used in their manufacture. X-ray diffraction, polarized light optical and environmental scanning electron microscopy (ESEM) with energy dispersive X-ray spectroscopy was used to study the composition. Mercury intrusion porosimetry was performed to obtain the total porosity and pore size distribution.

Adobe samples display a calcareous clay composition, with different proportion of clay minerals (27-39 wt%), quartz (21-45 wt%) and Ca and Mg carbonates (calcite 17-47 wt% and dolomite 2-11 wt%). Filosilicates are mainly kaolinite (24-34 wt%), smectite (31-46 wt%) and illite (20-45 wt%). Barium sulphate, various phosphates, iron oxides and hydroxides, bioclasts, pyrite, zircon and lithic fragments (Fig. 1) are also present. Iron oxides and iron hydroxides provides red and yellow colours.

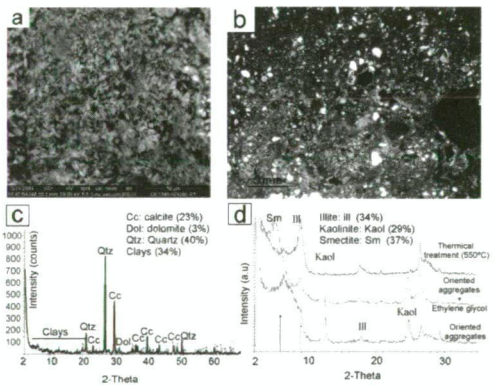

Fig. 1: Characterization of adobe. a) ESEM image; b) Polarized light microscopy image; crossed nicols; c) XRD of bulk sample; d) XRD of clay fraction.

Clay samples are very similar to the earthen materials and they could have been used as raw materials mixed with clays and sands from other geological sources (continental, fluvial and marine). The natural presence of roots and stems of plants, the cementation reactions of carbonates and silicates and intentional addition of grog (ceramic fragments) and organic materials in the clay paste could have improved the natural properties of the ceramic paste. Clays from the earthen pavement display white-yellow color (due to carbonate and hydrated iron hydroxides) being probably selected with aesthetic purposes. Difference in porosity between adobe and clay samples indicates compaction of the clays, with the consequent reduction in porosity and decrease in the pore sizes.

Understanding earthen construction methods and raw material selection has significant implications for understanding either the selection of settlement sites or the labour required to build in specific settings not directly adjacent to suitable raw materials [1]. These studies provide new insights to the knowledge of Phoenician construction techniques, since there are few or no other references available.

Acknowledgements: to ArqueoEstudioS. Coop. for providing the samples and collaboration. We are also grateful to the financial sources Geomateriales (S2009/MAT-1629) and Consolider (CSD2007-0058).

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The building materials of Koule Castle, Heraklion, Crete (Greece)

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This work is a primary study of the architectural elements and corresponding building materials of the Koule Castle in Heraklion, Crete (Greece). The characterization of the building materials of a historic structure is a necessary part of a conservation study.

Eighteen core samples of rocks and masonry mortars have been extracted by the 13th Municipality of Byzantine Antiquities from different parts of the monument, in order to determine their physical and technical characteristics as well as their deterioration state. Their morphological characteristics, granulometry, specific weight, water absorption index, compressive strength, as well as the mineralogical composition and the included fossils species have been determined.

The building stones of Koule Castle are sedimentary rocks, excavated nearby and in the island Dia. In their majority, they are biomicritic breccias and limestone conglomerates and bioclastic limestones with various marine fossils. In particular, the north monumental part is built of Triassic limestones, breccias and coarse conglomerates. Biomicritic breccia limestones show the highest strength values and lower water absorption index compared with the bioclastic limestones.

The old mortars have been studied by optical microscopy, X-ray diffraction (XRD) and scanning electron microscopy. Their examination revealed that beach sand has been used as inert material.

In some representative old mortars particle size analysis by wet sieving was carried out, in order to determine the nature of their constituents and evaluate the inert to binder material ratio. These data are necessary for simulation - reproduction of these materials used for restoration. The sum of the 2 mm - 0.125 mm fractions is regarded as inert material, whereas the material finer than 0.125 mm is regarded as the binder [1].

At least three types of mortars were identified and considered as the construction mortars during the different construction- reconstruction periods. Their basic mineralogical components are: calcite, portlandite, brucite, magnesite, dolomite, quartz and plagioclase. The presence of calcite in the binder of the studied mortars is a result of the carbonation of lime. The presence of portlandite and brucite is probably associated with the absence of adequate carbon dioxide in the interior parts and at the lower parts of the castle surrounded by sea, thus prohibiting the formation of calcite and magnesium carbonate correspondingly. Furthermore, the presence of both portlandite and brucite indicate the use of dolomites and Mg-rich limestones for the binder production.

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Production and distribution centers of Serra-d'Alto-style pottery (4th millennium BC) in southeastern Italy

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The Serra d'Alto pottery is a pot production occurring in southern Italy during the 4th millennium BC [1]. The use of depurated clays and firing temperatures around 700-800°C [2] suggest the presence of advanced ceramic technology, where the thin solid walls and the medium-to-large size of the products offer pictorial support to complex painted decorations [2]. These are black, and characterized mainly by spiral to meandrous motives with symbolic meaning. The Serra d'Alto style ceramic production coincides with a period of significant changes overall southern Italy, especially Apulia. The change to a hot-arid climate developed during the 4th millennium brings with itself the collapse of village agricultural civilization and the development of mobile communities of shepherds invading internal areas to find new pastures. Pottery is found in both cultural areas, thus not only in the villages, where it was presumably produced (need of depurated clays and appropriate ovens etc.), but also in internal sites such as caves. This testifies changes in the economy that involve population mobility and distribution of artifacts to mobile communities [3].

The archeometric study of a series of samples allows to define the production centers of Serra d'Altro ceramics and to follow the commercial distribution along the transhumance ways used by the ancient shepherds [4]. Together with the distribution of marine shell, the Serra d'Alto ceramics represents the oldest testimony of an exchange economy in Neolithic Italy. During the study, we evaluated technological aspects such as firing temperature, production and preparation of clay support, decoration and refining, all data indicating the state of art reached by the Neolithic workers [5,6]. The ceramic objects have been analyzed by OM and XRD for the minero-petrographic characteristics and by XRF and EDS/WDS for the chemistry. Moreover, a sampling of clays located near the ceramic production centers has been undertaken to establish a relationships between occurrence of the artifacts and local geology. The locating of clay extraction areas bears importance in reconstruction of the economic evolution in the 4th millennium BC.

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Mineralogical and geochemical study of coloured and white marbles from Spain and Portugal in the provenancing of some marble artefacts from *Thamusida* (Kenitra, Morocco)

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First results of an archaeometric study carried out in order to asses the provenance of marble artefacts from *Thamusida* (Kenitra, Morocco) have shown that local raw material exploitation was very rare. Most of the archaeological artefacts come from classical marble areas (Greece, Turkey, Italy), but not all the Mediterranean sources were successfully determined. Considering the possibility of a commercial exchange between Mauretania Tingitana and Betic and/or Lusitanian Roman Provinces, we focused our study on various types of marbles from those regions. Here, we present the results of a minero-petrographical and geochemical study on some of these marbles. The data obtained, combined with those already available from literature, represent a reliable basis for comparison with the undetermined artefacts. The marbles were collected from the Ossa Morena zone, including the Estremoz anticline (Spain-Portugal), and from Malaga and Almeria districts in the Betic chain (Spain). The specimens were investigated by XRD to detect the carbonate mineral type as well as by geochemical analyses to determine the carbon and oxygen stable isotope composition. OM observation and SEM-EDS analysis were carried out only on a representative selection of samples to find out the main textural features and the accessory mineral contents. We distinguished calcitic and dolomitic marble varieties. Dolomitic marbles mainly belong to Malaga district, but are sporadically present in other Spanish marble deposits.

The accessory minerals are quartz, plagioclase, muscovite/illite, phlogopite, Fe-Mg chlorite and tremolite (Viana do Alentejo, Almaden de la Plata), apatite, Fe and Ti oxides, titanite and Fe-sulphide. Dolomitic marbles usually have a scarce accessory mineral content, consisting of quartz and calcite. The geochemical data were reported in two different $\delta^{13}C$-$\delta^{18}O$ diagrams for Ossa Morena and Betic chain marbles. The isotopic values of Ossa Morena quarries overlap, mainly in the ranges $\delta^{18}O$: -9 and -5‰ VPDB and $\delta^{13}C$: 0.5 and 3‰ VPDB. The isotopic values of betic marbles fall in the range $\delta^{18}O$: -8.83 and 0.27‰ VPDB and δ^{13} C: 1.26 and 4.28‰ VPDB.

A preliminary comparison between the artefacts and the studied materials provided interesting results. The Malaga provenance seems highly probable; the Estremoz or Ossa Morena Almaden de la Plata quarry provenances are still uncertain. More analyses are needed to address the open questions and clarify the development of the commercial exchanges between Spain, Portugal and Morocco during Roman times.

Major element composition of Transylvanian gold: can it be used for archaeological provenance studies?

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Transylvanian gold is related to both epithermal ore deposits and their associated placer deposits in the Southern Apuseni Mountains (Romania). The primary deposits were formed during the Neogene volcanic event. Tens of economically-important ore deposits are concentrated in an area of about 900 km^2 known as the "Gold Quadrilateral" - a major source of gold for Europe throughout history. According to historical records, gold mining in Transylvania spans over more than 3,000 years. Between 1500–2000 t of gold were estimated to have been extracted in the Apuseni Mountains since prehistory [1].

Archaeological provenance studies are generally based on comparing the composition of the artefacts with that of the potential raw materials. No general consensus was reached yet concerning the most reliable correlation factors in the case of gold. As a first approach, we chose major elements chemistry and electron microprobe (EMP) measurements. Eight samples from the collection of the Museum of Mineralogy, Babeş-Bolyai University were selected: five samples from Roşia Montană (RM) (Fig. 1) and three from other historically-significant deposits: Trestia (T), Musariu (Mu), and Măgura (Ma). RM deposit is hosted by dacites, while the others by andesites [2].

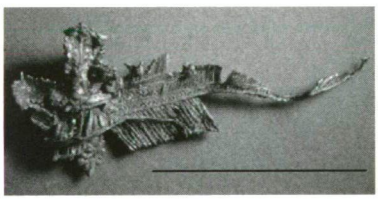

Fig. 1: Dendritic gold crystals from Roşia Montană, one of the IMA2010 logos (scale bar: 1 mm).

Au, Ag, Te and Cu contents have been measured. Based on 164 point EMP analyses, three compositional groups were outlined: a) low- (RM), b) medium- (RM, Mu, Ma), and c) high-Ag content (RM). Mineralogically, only the first group can be defined as gold, the other two are electrum (the full range of fineness is 577 to 875). For all groups, the same trend could be observed: whereas the Ag content is constant, Te (0.06–0.2 wt.%) and Cu (<0.02 wt.%) substitute Au. RM gold shows a remarkable compositional variability, ranging from $Au_{0.43}Ag_{0.57}$ to $Au_{0.79}Ag_{0.21}$. Thus, samples with the same origin plot into different groups, while those originating from different deposits plot in the same narrow compositional field (b).

Summarizing, the major elements in gold cannot be used for chemical fingerprinting, but EMP proved to be suitable for deciphering chemical mechanisms at micrometer scale. However, for gold provenance studies, hierarchical cluster analyses on larger sets of data for major, as well as trace elements and isotopes studies are required.

Acknowledgements: The study was supported by ID-2241 project funds (Romanian Ministry of Education).

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Mineralogical-geochemical characteristics of the mammal skeletal remains from the selected archaeological sites in Poland

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We have studied bones and teeth of woolly mammoths (*Mammuthus primigenius*) from the site Spadzista Street (B) in Krakow and bones of cave bears (*Ursus spelaeus)* from two caves (Bisnik and Nietoperzowa) in Southern Poland. The materials were studied using SEM-BSE, XRD, and FTIR methods. Samples from Spadzista Street and Biśnik are quite well preserved, in contrast to Nietoperzowa cave where only fragments of bones few centimetres long were found. In scanning electron microscope their histological structures (osteons, bone trabeculae, enamel prisms, dentine canaliculi) are easily seen. The studied skeletal remains are built of carbonate-rich apatite-(CaOH). The crystallinity indexes (calculated after Person et al. [1]) are rather low: 0.03-1.14 in woolly mammoth samples, 0.1-0.21 and 0.02-0.15 in cave bear samples from Biśnik and Nietoperzowa caves, respectively. Only in enamel the crystallinity indexes were much higher: 0.67-0.78 in woolly mammoth and 0.95 in cave bear samples. The typical range of Ca/P mole ratios of fresh bones is 1.59-1.67 [2]. The average ratios, calculated from EDS analyses of the studied samples, are different: mammoth bones - 1.92, cave bear bones from Biśnik and Nietoperzowa caves - 1.73 and 1.23, respectively. The higher values can be caused by replacement of PO_4^{3-} groups by CO_3^{2} and/or enrichment in Ca^{2+} ions which is not surprising because of common presence of calcite in those bones. The lower values can result from a decrease of CO_3^{2-} in apatite, which is one of the common diagenetic processes [3]. There are some differences in secondary minerals infillings between cave bears and woolly mammoth remains. In the bear bones Haversian canals are usually not infilled with minerals, only occasionally calcite is present. Fe-Mn (hydroxy)oxides coat or infill both the osteocyte lacunae and the dentine canaliculi. In addition, in the bones from Nietoperzowa Cave manganese is sometimes present in a form of dendrites. In the woolly mammoth remains Haversian canals, bone trabeculae and cracks are commonly infilled with calcite or carbonate sediment. The dentine canaliculi are coated or infilled with secondary apatite. The Fe-Mn (hydroxy)oxides are present occasionally in osteocyte lacunae. It is worth to note that in woolly mammoth bones the bacterial alterations were found. In some samples they are very common, whereas in the cave bear bones we have not found any microbial changes. It seems that differences between studied bones are caused by different burial environment.

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Iron age pottery from Garvão votive site (SW Iberia) – an interdisciplinary study

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The Iberian Peninsula was a highly sought after area in ancient times due to its abundance in geological resources. Hence, the Iberian Iron Age was a period of successive social and political transformations, sometimes resulting in conflicts. These began with the earliest Celtic invasions (or migrations) that imposed a strong continental influence in Iberia against the oriental inspired societies like the Tartessos kingdom. The movement of these populations toward south is constant throughout the entire period. Simultaneously, the Semitic civilizations (i.e. Phoenician and Punic) control was maintained in south Iberia through the presence of autonomous cities with strong commercial and cultural connections to the Mediterranean. This political framework was broken in 218 AC by Romans disembark in the context of the second Punic war.

In this general context, at around 200 AC, Garvão probably belonged to the Conii territory corresponding to the current SW Portugal or "Baixo Alentejo" and the western Algarve. It is believed that this region, although inhabited by populations of Celtic origin, was characterized by a very strong Mediterranean cultural influence. It seems that Garvão was an important Iron Age II holy site where an impressive votive deposit was discovered. The materials recovered (mainly pottery) were intentionally deposited, carefully arranged in order to optimize the available space.

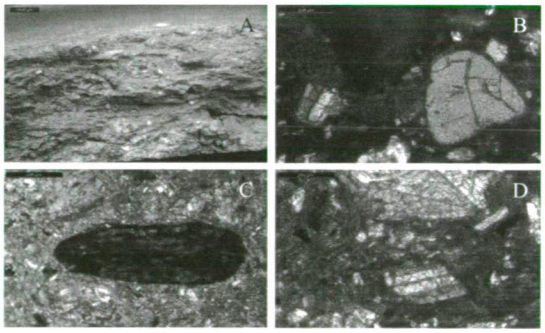

Fig. 1: Iron-age Garvão pottery. (A) Chromatic heterogeneity in cross section. (B) OM micrograph NX. Plagioclase and rounded quartz in black matrix, (C) OM Micrograph NX. Ceramic fragment. (D) OM Micrograph NX. plagioclase in red matrix.

A detailed study of the pottery based on stylistic analysis was carried out allowing the classification into different clusters. As the ceramics mineralogical and chemical composition depends also on technological know-how and social environmental parameters, a combined analytical approach was adopted to characterize the pottery samples by means of Optical (OM) and Electron microscopy (SEM + EDS), Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray Diffraction (XRD). The combination of these techniques applied to selected Gãrvao pottery allowed the recognition of the ceramic phase composition, firing temperature, kiln atmosphere, ceramic manufacturing processes and origin of raw materials.

The chemical and mineralogical results suggest that the Gãrvao region was characterised by strong connections both with Mediterranean as well as with local production areas reflecting its role in ancient times as a rich and important multicultural centre.

On the use of Earth Materials in SW Iberia mortars – an historical perspective

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Traditional and historic mortars are composite materials consisting of a binder (usually lime or hydraulic lime), aggregates (quartz sand, calcite or dolomite) and some additives (e.g. brick dust, volcanic ash) in order to increase adherence, workability, strength and durability [1]. The characterization of mortars allows the identification of their phase and chemical compositions and the characteristic features related to the physical properties. Moreover, sometimes it is possible to identify the alteration products and, in some cases, establish the provenance of materials used in the manufacture of mortars [2].

Thus, the study of the ancient mortars composition, using techniques of chemical, mineralogical and microstructural characterization, plays a major role in the preservation of cultural heritage, guiding all actions for the conservation and restoration. On the other hand, it gives a very deep knowledge about the techniques of construction, previous repairs and their performance. This type of information is likely to be historically integrated, contributing to the knowledge of the societies that constructed the buildings.

The similarity between traditional mortars and sedimentary clastic rocks are evident (Fig. 1). In both, it is possible to figure out cement that sustains together the clasts (in sedimentary rocks) or the aggregates (in mortars). Nevertheless important differences are obvious. Additives are frequently present in order to get better mechanical properties and the very alkaline environments during the merging of the lime and the aggregates cause frequently the partial dissolution of quartz aggregates.

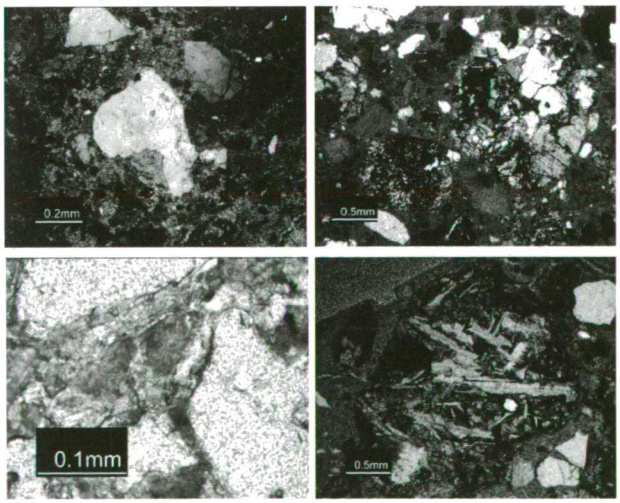

Fig. 1: Microphotos of Southwest Iberia ancient mortars. A-Concufate villa (Roman), B-Evora (Medieval), C- Elvas (16th century), D-Lisbon (18th century). A, B – crossed polarizers; C, D – one polarizer.

Methods like XRD, TGA, optical microscopy, SEM-EDS and chemical analyses techniques are currently employed. The results can be assigned to the society's capability to manage technology and to access and select raw materials. Over the past few years research applied to roman, Islamic and medieval mortars will be revisited and an evolutionary trend to the use of earth materials in SW Iberia mortars will be presented.

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Rock crystal artefacts and determination of their provenance

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In Central Europe, there are numerous archaeological sites from which chipped rock crystal artefacts are known. The raw material is commonly considered of Alpine region provenance. However other possible sources could be mentioned in other areas (Fig. 1). The most important places are located in the Bohemian Massif, especially in the Moravian Moldanubicum (Sklené – Rousměrov SE of Žďár nad Sázavou and the vicinity of Brtnice), and there are proofs of their prehistoric exploitation. Another source area becomes evident in the Silesicum (Jegłowa near Strzelin, Žulová). We record also rock crystal sources in the Austrian Moldanubicum or within Lower Carboniferous rocks in N Moravia (Bílovec) [1].

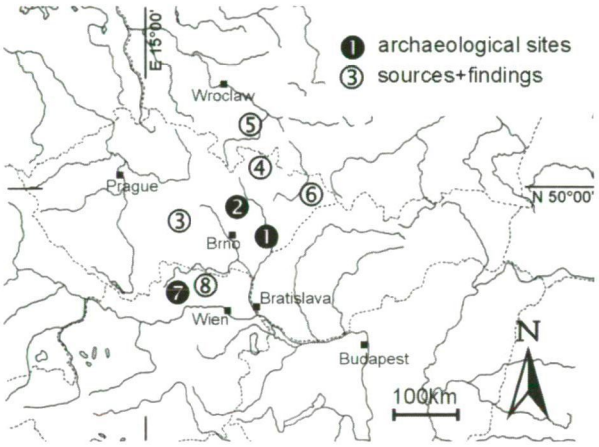

Fig. 1: The major occurrences of rock crystal sources and findings of artefacts. Sites: 1 – Nová Dědina, 2 – Žitného cave, 3 – Sklené, Brtnice (Moldanubicum area), 4 – Žulová area, 5 – Jeglowa, 6 – Bílovec, 7 – Gudenushöhle, 8 – Nödersdorf.

Microthermometry, Raman spectrometry and some other techniques have been applied on material from the Paleolithic (Aurignacian) site Nová Dědina (ND, no. 1 in Fig. 1) where several hundreds of rock crystal chips have been discovered and compared to the mentioned sources. The used methods, based on the investigation of fluid inclusions, can be considered as a model for progress in further research.

Fluid inclusions (FI) represent defects (cavities) in crystal lattice, being filled with liquids (L), gases (V), and solids (S). Trapped and sealed parental fluids in primary inclusions are regarded as isochoric systems telling story on genetic conditions at particular places. If we are able to decipher the genetic information from the fluid inclusions of the "lost" material (with unknown provenance) we have a chance to find the site of origin. The most important petrographic aspects have been revealed within FI assemblage from ND. Two types of 3-phase inclusions L+V+S1+S2 and L1+L2+V and their fluid properties enable to exclude the sources from the Alps, Silesicum and northern Moravia. Fluids nature coincides well with sources from Moldanubicum with pegmatite signature.

The used combination of genetic parameters, both from natural sources and archaeological sites, is a very sensitive methodological approach how to select and define the provenance of rock crystal raw material.

Acknowledgements: Our investigation has been supported by the research project MSM0021622427 and grant Kontakt 6-06-11.

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Pietra ollare artefacts from Červar Porat (Istria, Croatia): composition and possible origin

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During archaeological excavations performed between 1976 and 1980 at a Roman villa rustica in Červar-Porat located close to the town Poreč (Istria peninsula, Croatia), among other Late Antique period fragments (glass, metal, ceramics), fourteen peculiar stone vessel fragments were discovered. They show characteristic tracks of the manufacturing by means of lathe. Vessels made by analogous processes from similar materials have already been found at several localities at Croatian Adriatic coast, but no systematic mineralogical study on this kind of material was performed so far.

Two of these vessel fragments were recently investigated in more detail by mineralogical methods. The first one (inv. no. 7912) is greenish-grey in colour (Fig. 1). X-ray powder diffraction revealed that the only constituent of this fragment is a chlorite group mineral. The mineral composition together with visible schistosity indicates that source material was chlorite-schist, a low–grade metamorphic rock. Such material is one of different lithologies included by Italian term *pietra ollare* and German *Lavez*.

The other fragment (inv. no. 7907) is dark greenish-grey on the fresh broken surface and brownish on outer and inner vessel surfaces. Distinctive bronze coloured flakes can be seen in some parts. The fact that XRD pattern of the second fragment was similar to the XRD pattern recorded on the material from the first fragment after heating to 1100°C indicate that the second vessel was most probably used for cooking, and during that process it was exposed to elevated temperatures.

Fig. 1: Vessel fragment (inv. no. 7912), 8 cm wide, showing tracks of manufacturing by means of lathe.

In order to determine possible origin of analysed fragments their mineral and chemical composition was compared with those recorded for samples collected in Valle d'Aosta and Valli di Lanzo (north-western Italy) and literature data for *pietra ollare* originating from other localities in Italian Alps.

Mineralogical and experimental study by FTIR of archaic ceramics from Amathous (Cyprus)

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Many ceramics of the archaic period have been found in the archaeological Amathous site, southern Cyprus (Fig. 1). Previous studies on these ceramics indicated a good agreement between chemical analysis and the typo-chronological classification [1]. However a geological survey and an experimental study were required in order to complete these data. The aim was to localize sources of raw materials (clay and temper) and to understand the manufacturing methods, especially firing processes.

The infrared spectroscopy and X-ray diffraction have been used to characterize 44 materials sampled around Amathous, 10 ceramics fragments and the results of firing experiments.

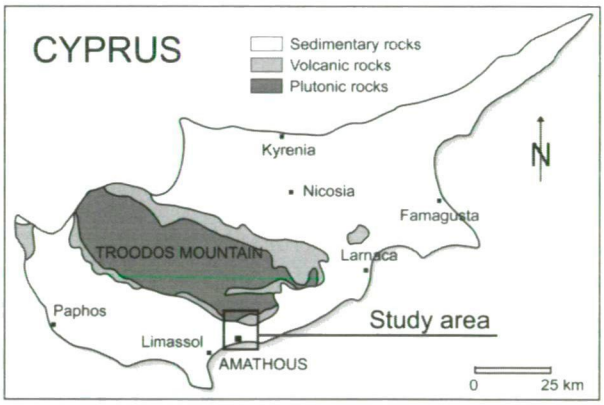

Fig. 1: Study area location within Cyprus territory

The Cretaceous marine clay ("Moni formation") and the black basaltic sand from the beach west of Amathous (used as temper) were identified as the source of raw materials. In addition, firing experiments show that ceramics were fired at 650°C (Fig. 2). The red-fabric pithoi ceramics were made from the same materials but firing temperatures are higher than 650°C.

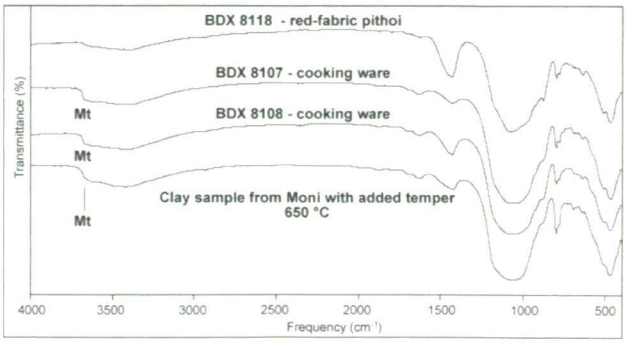

Fig. 2: Cooking ware and red-fabric pithoi spectra. Comparison with the spectra obtained through experimental firing of raw material samples.

[1] Fourrier, S. & Hermary, A. (2007) *EtChypr* XVII.

Characterization and provenance of building stone from Notre-Dame-de-Grâce, Sérignan (southern France)

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The restoration project of Notre-Dame de Grâce church (Sérignan, southern France, Fig. 1) was accompanied by a detailed study of the building materials. The aim was to characterize the various lithologies, their repartition on the frontage (linked or not with reconstructions and restorations) and their origin. Some substitution materials were also sought.

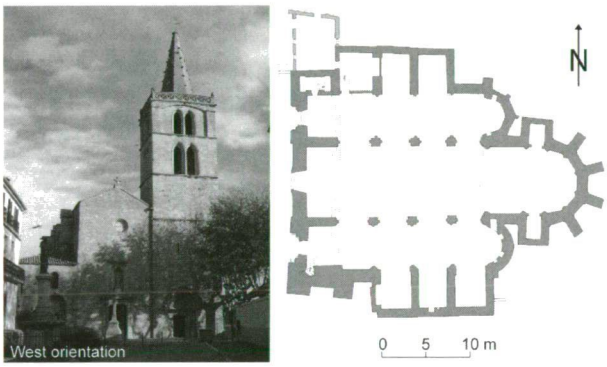

Fig. 1: Notre-Dame de Grâce: photography and plan (© Cabinet D. Larpin).

The macroscopic and microscopic investigation of 25 samples from the edifice permitted to characterize 5 different stone types: 1) bioclastic limestone, 2) sandy limestone, 3) Ostrea-bearing limestone, 4) red-algae-bearing limestone and 5) fine-grained limestone. All these materials were formed in the carbonate shelf during Miocene.

The (1), (2) and (3) limestones correspond to the most voluminous monument blocks and have a local origin. They are found in old quarries around Sérignan and Béziers (Fig. 2). The (4) and (5) types were respectively used for mullions of the church windows and for the four pillars of the western frontage. This two rock types originate in the still exploited quarries of Beaulieu (4) and Fonvieille (5) (Fig. 2).

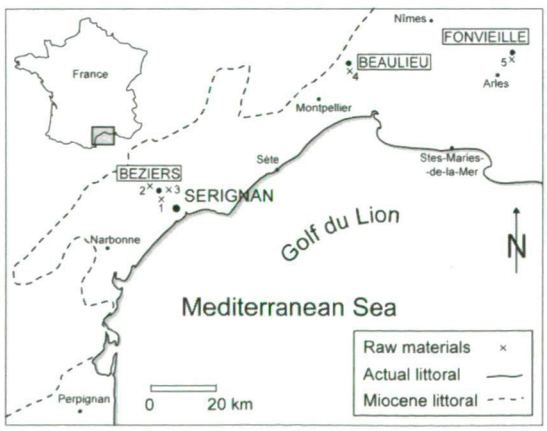

Fig. 2: Source of building materials used for Notre-Dame-de-Grâce, Sérignan. The insert in upper left shows the position of the map within France territory.

Traditional earthen building materials in the Western Himalayas

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The Tibetan mountain village of Nako in the Indian Western Himalayas houses a Buddhist monastery temple complex dating from the 11th - 12th centuries, which reflects both significant aspects of Tibetan artistic and cultural history as well earthen building traditions. Within the "Nako Project" dedicated to saving the endangered temple buildings, the "Scientific study of the Artwork at Nako, India", funded by the Austrian Science Fund (FWF), addresses local clay raw materials used for the historic temple structures and in recent local building practice. The soils THAWA, TUA and SASSA make up the building materials, the adobe, joint mortars and plasters, as well as the supports of the sculptures in the four temples.

THAWA, meaning "earth" in local Bhoti language, consists mainly of poorly sorted, gravel- and sand-sized detritus derived from granitoids of the High Himalaya crystalline. THAWA has a yellowish brownish colour. The clay content, and thus its plastic component, is low. It is composed of quartz, K-feldspar, albite and abundant mica. The mineralogical composition suggests a granitic parent rock. The predominant clay minerals of the fraction < 2 µm are illite/muscovite and chlorite, both of detrital origin. Small amounts of kaolinite and traces of vermiculite occur. The plasticity index is low, the shear strength is rather high.

TUA is most likely a fine-grained deposit of a glacial lake. It is light grey in colour. The silt- and clay-content of TUA is high, which gives better plasticity properties, also expressed by a higher plasticity index. The bulk rock mineralogy consists of calcite, quartz, mica, chlorite and little feldspar. The clay mineral assemblage of illite/muscovite, chlorite and low amounts of kaolinite is very similar to THAWA.

SASSA is a greenish white, well-compacted, unstratified deposit, resembling a till. Similar portions of gravel, sand, silt and smaller amounts of clay produce extremely poorly sorted sediment. Varying amounts of dolomite, calcite, amphiboles and pyroxenes are the main constituents of the bulk mineralogy. Besides illite and kaolinite in traces, the predominant clay minerals are a mixed layered smectite/chlorite and/or a smectite. SASSA shows the highest plasticity index and the lowest shear strength of the three types.

Adobe, joint mortars, plasters, and sculpture supports show similar grain size distributions and similar mineralogical compositions. They consist of a mixture of THAWA and TUA and plot along a line indicating a mixing ratio of 4:1, which is still used as a recipe for plastering, passing on the tradition of the old building history of the temples. Additionally, fibres deriving from plants, animal hair and skin, ash, as well as proteinaceous binding materials were found admixed to the local soils in order to improve the strength and plastic qualities of the historic building and support materials. The use of organic additives correlates with Buddhist literature sources. SASSA, nowadays used as water resistant coating for indoor walls, was detected only in one case of a later sculpture repair.

Raman spectroscopic study of ancient potteries in Thailand: Wiangkalong pottery samples

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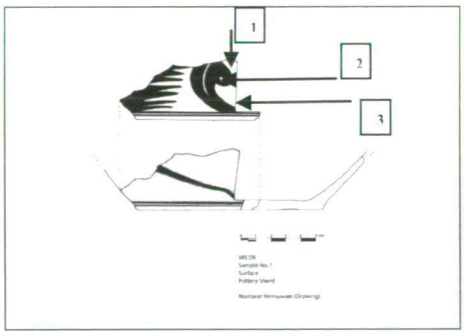
The aim of this work is to explore the potential of Raman spectroscopy in assessing the chemistry and mineralogy of ancient potteries from Wiangkalong, a major ceramic-production city in northern Thailand, once colonized by the ancient Lanna Kingdom (1296 AD). Potteries from such locality were produced with shapes and designs resembled those of the Chinese Yuan and Ming Dynasties. Fragments of the pottery samples from Wiangkalong were analysed for the first time. Characterizations of clay minerals were also carried out using X-ray diffractometer and scanning electron microscope equipped with energy dispersive X-ray fluorescence spectrometer. These instruments in combination have been proved to be useful in archaeological science research.

The experiment results showed the peculiar components of ancient ceramic bodies. As for an example, the result of corresponding Raman spectra probed at specific areas on a fragment of an ancient bowl showed different absorption patterns (Fig. 1). This reflects the differences in matrix compositions, both chemically and mineralogically, of the areas measured. The research results based on instrumentations mentioned above showed that the body matrix mineralogy of the Wiangkalong potteries is highly heterogeneous, suggesting the presence of large variety of minerals and trace elements in the clay, as well as the variable conditions of firing control.



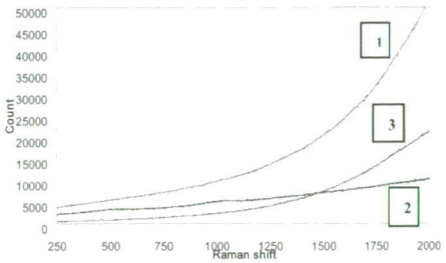


Fig. 1: Wiangkalong pottery fragment (upper image), and the Raman spectra corresponding to the specific areas pointed as 1, 2, and 3, which are the enamel, the flower muster, and the matrix respectively (lower image).

Deterioration of the Sasov castle (Slovakia) and replacement material for the weathered building stone

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The Sasov castle in Middle Slovakia belongs to the cultural heritage, being one of the national monuments. The ruins of the medieval castle on a volcanic hill above the Hron River are a characteristic landmark, 4 km SE from the town Ziar nad Hronom. In 1997 the condition of the buildings was documented. In a revision after 12 years, the comparison with the previous documentation revealed the fastest deteriorating parts. Searching for the reasons, an engineering geological map of the castle hill was created, showing the relation of tectonic faults and slow slope movements (tilting) with cracks in the masonry and some collapsed walls. Most of the cavities and overhangs in the remaining masonry are due to the weathered binder. Intensive weathering of the building stone, studied within the project VEGA 1/0413/09, caused other reasonable part of the damages.

The masonry is built mainly of Neogene andesite, which is common in this area, as part of the volcanic Stiavnicke Vrchy Mts. More altered highly macro-porous stones show some yellowish-brownish coatings on the surface and fissures. The comparison of some better preserved building stones with the rock in an old local quarry showed a very good match in the properties (mineral assemblage, colour, porosity, strength) with the most altered parts in the rock mass. The accessible but more weathered rock of the upper part of the quarry was exploited as first for the castle. Exposed to environment on the castle hill without any cover, it disintegrates faster than in the rock mass. Volume changes due to smectite swelling as well as freezing-thawing processes in the effective pores probably enhance the deterioration. The most altered building stones are almost white and disintegrate into sand. But there, the X-ray diffraction indicates the possibility of other source or an epiclastic origin.

The sound quarry stone is an andesite of dark grey colour, from medium-grained to aphanitic texture, micro-porous, and extremely strong. Results of the X-ray powder diffraction showed that the mineral assemblage is dominated by andesine (62 wt%) and amorphous phases/glass (27 wt%). As minor phases, augite (8 wt%) and magnetite (3 wt%) were identified. With increasing alteration, smectite content is increasing up to 22 wt%, while augite, magnetite and amorphous phases are decreasing. A considerable part of the macro-pores is the result of selective leaching of weathering products, even when some of the macro-pores are primary voids, caused by the rapid cooling of the melt near the surface. Comparison of the sound rock with the altered one shows an increase in total porosity (from 2.4% to 21.2%) and in effective porosity (from 2.2% to 15.0%). There is a clear relation between the porosity and smectite content on one side, and the uniaxial strength (tested by the Point Load Test) on the other side. The strength dropped from 270 MPa to 51 MPa for more weathered macro-porous stone. Enlin-Neff tests on rock powders proved higher water adsorption in the weathered rock mainly due to the smectite content.

For any castle reconstruction, sound stone from deeper parts of the quarry can be taken as replacement material. It promises better durability, good mechanical properties, as well as acceptability from a historical point of view.

Incorporation of fine and coarse sepiolite in lime-metakaolin mortars

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The aim of this research was to assess the behaviour of fine and coarse sepiolite acting as water reservoir in lime-metakaolin mortars for applications in building rehabilitation. With this purpose three sets of mortars were prepared: a) mortars with 1:3 air lime (AL): sand volumetric ratio, in which lime binder was replaced by 10% and 20% of metakaolin (MK, commercial product, Portuguese origin); b) the same mortar compositions in which air lime was substituted by 5% of i) fine sepiolite (S, average particle size 2.4 μm, commercial product, Spanish origin), ii) coarse sepiolite (CS, particle size within the range 0.3-1.2 mm). Samples were cured for 28 days according the EN 1015-11 standard.

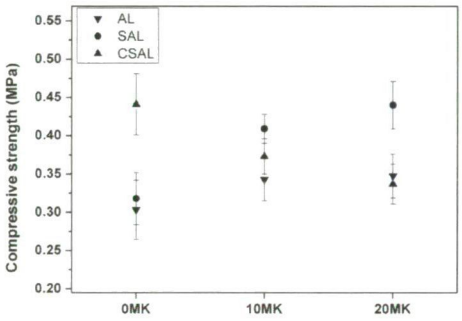

Fig. 1: Compressive strength (MPa) of mortars.

The obtained results showed the increase of mechanical properties in AL-metakaolin mortars when compared to AL-mortar, as well as the improvement of flexural and compressive strengths with the addition of metakaolin content (Fig. 1). Compared to AL mortar, flexural and compressive strengths increased 20% and 12% for AL-metakaolin mortars, respectively. New calcium-silicate and calcium-aluminium-silicate mineral phases were identified in mortars containing metakaolin, which result in higher mechanical strength in metakaolin-blended mortars.

As expected, the fibrous habit of sepiolite caused enhanced conjugation with the individual components and comprehensive compatibility in the mortar system. Considerable improvement is related to fine sepiolite-AL-metakaolin mortars, where compressive strength increased 24% in comparison with AL-metakaolin mortars, while 6% enhancement is associated with addition of sepiolite to AL mortar without metakaolin. It is a consequence of high specific surface area and absorbent properties of sepiolite. The incorporation of coarse sepiolite in AL mortar raises the compressive and flexural strength, by 47% and 52% respectively, compared to AL mortar. On the contrary, the presence of coarse sepiolite in AL-metakaolin mortars promotes a significant decrease of mechanical strengths. Phenolphthalein tests showed an improvement of carbonation rate with the addition of both fine and coarse sepiolite. In early ages, the addition of fines has a significant impact on mortar compressive strength. The fibrous structure of the fine sepiolite also has a possible positive outcome on mortar strength due to binding effect. The effect of chemical reactions, both carbonation and pozolanic reaction will be more evident at 90 days due to slow reaction rate.

Spanish sepiolite deposits

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Spain is the world leader in sepiolite production. Madrid hosts the world's largest sepiolite deposit with reserves estimated over 15 Mt of high quality material. The main Spanish producer is TOLSA (300 kt of sepiolite in 2008), which mines the main deposits, located in the Madrid basin (Vicalvaro, Madrid, and Cabañas de la Sagra, Toledo). SEPIOLSA produced 164 kt in 2002, from the deposits of Paracuellos del Jarama and Barajas (Madrid) and BENESA 70000 tpa in Valdemoro (Madrid). Another important deposit currently under exploitation is located in Orera, in the Calatayud basin (Zaragoza). MYTA produced 131 500 t from this deposit.

The Madrid Basin is a Tertiary basin developed during the Alpine orogeny. The Miocene sediments of the Madrid basin display a concentric facies distribution pattern. Close to the margins of the basin there are detrital sediments corresponding to alluvial fan systems. These sediments are predominantly arkosic to the NW and S, and litharenitic to the NE and E. Transitional facies correspond to mud flat environments between the detrital and lacustrine sediments. The lacustrine sediments are mostly evaporites. In the northern and southern margins of the basin, arkose sands dominate gradually passing to carbonatic paleosols and clays in the distal facies of the alluvial fans and in the lacustrine systems. These clayey facies include the important Mg-rich clay deposits.

At least seven layers (≥ 1 m thick) of lacustrine sedimentary rocks containing sepiolite can be recognized in the Vicálvaro-Barajas area east of Madrid [1]. The layers are up to 7 m thick in places, with a virtual pure sepiolite composition. The Vicálvaro sepiolite deposit covers a 7.5 km^2 area elongated in NW-SE direction (5 km long and 1.5 km wide), with maximum thickness 12-15 m in the center and progressively decreasing towards the borders of the deposit. Clay layers with variable colors dominate in this unit, intercalated with carbonates (marly mudstones, marls, dolostones, and limestones). In the southern area of the Madrid basin (Cabañas de la Sagra, Toledo) the sepiolite is located in an arkosic unit, (distal parts of alluvial fans). Clayey levels consist almost exclusively of sepiolite and trioctahedral smectites, with variable ratios between pure end members. At the top of the unit sepiolite is associated with dolomite and chert.

The deposit in Orera in the Calatayud basin (Zaragoza) currently exploited by MYTA develops in the marly-carbonate transitional facies of the Calatayud Tertiary lacustrine basin. It corresponds to an alluvial fan marginal deposit which during late Miocene closed a valley producing a lake in which sepiolite was formed. Sepiolite clays and sepiolite-palygorskite clays also occur in the Cuesta facies of the Duero Tertiary basin, and in Lebrija (Sevilla).

The sepiolite from Madrid basin has specific surface area ~270 – 330 m^2g^{-1}, and fibres longer than 10 μm in places Sepiolite from Calatayud has also high specific surface area (~270 m^2g^{-1}) and the size of the fibres is medium, generally smaller than 11 μm in lengh. The contribution of external and microporous surface area is similar in both cases.

[1] Leguey, S. et al. (1995) in Churchman, G.J., Fitzpatrick, R.W. & Eggleton, R.A. (eds.) *Clays: Controlling the Enviornment*. Proc. 10th Clay Conf., Adelaide, Australia, 1993, CSIRO Publishing, Melbourne, Australia, 383-392.

Distribution of layer charge of smectites in the Miloan bentonites, Aegean Greece

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Layer charge is a fundamental property of smectites which controls cation exchange capacity, ion exchange selectivity swelling and rheological properties. Within this context, determination of layer charge and charge distribution within a bentonite deposit is of particular importance because a) it can shed light on the formation mechanism of the bentonite and any possible subsequent modifications, and b) it controls the variability of bentonites in various industrial applications. This knowledge, in turn, can assist in an understanding why production of Na-activated smectites from Ca-Mg smectites usually yields unpredictable results.

Layer charge and charge distribution of smectites was studied in three bentonite profiles in Eastern Milos. The two profiles were 120 x 30 m long, whereas the third one was 200 x 45 m long and has been affected by contemporary solfatara spring activity along a NE-SW trending fault. The bentonites formed by submarine alteration of Lower Pleistocene pyroclastic flows. The deposits consist of Ca-smectite (60-95%) with subordinate quartz and/or traces of opal-CT. Minor calcite, kaolinite and K-feldspar are present in places. Determination of layer charge was carried out according to [1]. Briefly, the less than 2 μm fractions were separated by settling, saturated with K and dried on glass slides to make oriented clay mounts, which were subsequently saturated in ethylene glycol vapour at 60°C for 16 hours. The layer charge and charge distribution of smectites was determined by means of the LayerCharge program [1]

Although mineralogy is similar in the three profiles, the layer charge distribution follows different patterns. The first profile is characterized by a high charge anomaly (layer charge > 0.50 eq/phuc) in the lower WNW sector whereas the remaining profile is characterized by smectites with intermediate layer charge (layer charge 0.43-0.47 eq/phuc). The second profile is dominated by gradual increase of the layer charge towards the top of the profile, from 0.41 eq/phuc at the bottom, to 0.48 eq/phuc at the top. Moreover tetrahedral charge tends to increase towards the top of the profile. The third larger profile is dominated by a high charge bentonite layer ~ 12 m thick at the bottom (layer charge > 0.5 eq/phuc), followed by a thick layer > 30 m thick with layer charge 0.44-0.47 eq/phuc, which does not display certain trends. In the area affected by the solfatara spring activity the layer charge decreases (0.41-0.42 eq/phuc).

The different distribution patterns of layer charge in the three profiles reflect different evolution of the bentonites. In the first profile the high charge smectites are attributed to hydrothermal alteration which postdated the formation of bentonite and are associated with fine-grained K-feldspar and kaolinite. The distribution of layer charge in the remaining profiles reflects the geological environment during bentonite formation. The formation of low charge smectites in the vicinity of the solfatara spring is also attributed to contemporary hydrothermal alteration and intensive leaching of the original smectites

Acknowledgements: We thank S&B Industrial Minerals S.A. for their permission to sample their quarries.

[1] Christidis, G.E. & Eberl, D.D. (2003) *Clays Clay Miner.*, **51**, 644-655.

Sustainable use of fines from the sand and gravel industry

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In 2008, some 260 million tons of sand and gravel were produced in Germany [1]. During processing sand and gravel are split into different grain size fractions. Fines are separated by washing and screening and usually dumped as water-sediment suspensions in tailing ponds close to the quarries. Up to now fines are rarely used in industry, e. g. as aggregates to produce bricks and tiles [2]. Pflug (2001) estimates that about 50 million tons of fines are produced in Central Europe every year [3]. The aim of the study is to determine the qualitative potential of fines from the processing of sand and gravel in Germany for applications in the brick and tile industry.

Fines were sampled in 28 sand and gravel pits all over Germany. After the particle size analysis the mineralogical and chemical composition of the fines were determined in the laboratories of the German Federal Institute for Geosciences and Natural Resources. As a result, 12 samples with an average grain size >200 µm, low clay mineral content or high concentrations of carbonates were rejected due to the fact that they cannot be used in the brick and tile industry.

The mineralogical composition of the remaining 16 samples is presented in Table 1. Four samples are dominated by kaolinite (samples 1, 7, 11, 16) and one by illite/muscovite and an expandable mixed-layer mineral (sample 4). In general, the selected samples consist of different mixtures of quartz, feldspar and a wide variety of clay minerals, carbonates, and oxides (Table 1).

Table 1: Simplified mineralogical composition of selected samples (I/Sm/M-L=illite/muscovite, smectite and mixed-layer minerals, K/Ch=kaolinite and chlorite; Q=quartz; F=feldspars; C=calcite and dolomite; Ox=Fe-oxihydroxides and Ti-oxides; O=others)

	I/Sm/ M-L	K/Ch	Q	F	C	Ox	O
1	15	35-40	35	10	-	<5	<1
2	15	5	45	15-20	10	6	<5
3	20-30	10-20	10-20	10-20	10-20	<1	<1
4	40-50	5-10	20-30	20-30	-	<1	<1
5	15	-	50	15-20	10-15	5	<1
6	15	5	40	30-35	5	<5	<1
7	15	30-35	40	10	-	<5	<1
8	25-30	20	15-20	25-30	<1	5	<1
9	20-25	5-15	25-30	15-25	-	<5	<1
10	10-15	5-10	70-75	5	-	<5	<1
11	-	55	40	-	-	5	<1
12	15	-	45	35	-	<5	<1
13	15	5	55	10-15	<10	5	<1
14	20	10	20-25	10-15	25-30	<5	<5
15	15-20	5-10	30-35	25-35	<5	<5	<5
16	25	45	20	10	-	<5	<1

The chemistry and the mineralogy of the fines reflect the composition of the source rocks the sediments derived from. A regional distribution of different qualities within Germany was not identified.

The ceramic properties of the samples will be discussed and the potential uses of fines in the brick and tile industry estimated.

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Bentonite deposits of Hungary – a review of their mineralogy and geology

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In the Hungarian part of the Pannonian Basin several bentonite deposits of some recent or historic economic importance are known (Mád-Sima, Mád-Újhegy, Istenmezeje, Komlóska, Pétervására, Salgótarján-Kazár, Budatétény, Sóskút, Egyházaskesző, Gérce). Some of these are being exploited in our present days. This summary gives details of their mineralogy, geochemistry and geology.

Most of these deposits are related to Neogene volcanic areas. These activities are marked partly by submarine pyroclastic accumulations and coeval andesitic lavas of Carpathian age (~17.5–16.2 My), followed by Badenian (~16.2–13 My) pyroclastics and associated basaltic, andesitic, rhyodacitic and rhyolitic flows. In the Late Miocene to Pliocene/Pleistocene period (~12–2 My. in the western Pannonian Basin) alkali basalts have been produced, associated by lacustrine sediments.

The bentonites derive from different alteration styles of volcanic rocks:

- Primary, syn-volcanic bentonitisation: halmyrolitic and hydro-diagenetic (Tokaj Mountains), maar lake bentonites in W-Hungary (Egyházaskesző, Gérce).
- Secondary processes: these secondary bentonites are the results of intense argillization around hydrothermal centres in several parts of the Tokaj Mountains (Komlóska).
- Tertiary processes: are characterized by erosion and re-deposition in isolated marine gulfs and lagoons (e.g. Istenmezeje, Budatétény) or re-worked deposits in post-volcanic warm-water geyser lakes (e.g. Mád-Sima and Mád-Újhegy).

In general these bentonites are characterised by the dominance of the montmorillonite (Ca, Ca/Na, Fe), with small amounts of quartz, cristobalite, feldspars and biotite. Also in few cases are presents beidelite (Fe), kaolinite and mixed-layer clay minerals (rectorite) at Mád-Újhegy, and vermiculite/smectite at Egyházaskesző-Gérce.

Their swelling capacities vary in wide range, few bentonites are not activated (e.g. Kazár). Chemically these bentonites are resulted from argillization of rhyolitic-rhyodacitic, and basaltic pyroclastic rocks (Fig. 1).

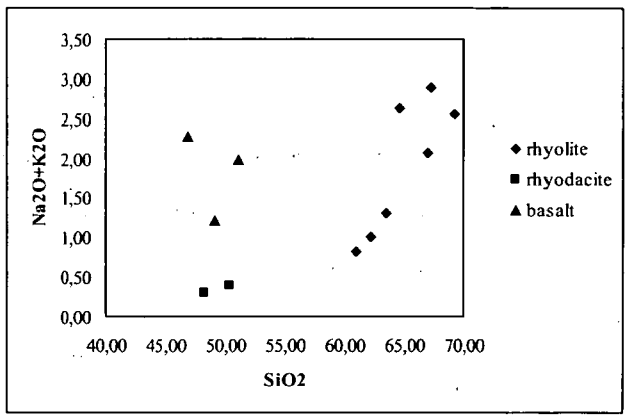

Fig. 1: Na_2O+K_2O vs SiO_2 diagram of bentonites from different pyroclastic rocks.

Natural pigments in clayey sediments of Kuprava pit in Latvia

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Clayey pigments are relatively easy to obtain, therefore they have been used since prehistoric times for painting and decorating of bodies, ceramics, cave walls and temples. Despite utilization and research of natural pigments not much is known about their origin, chemical, physical and mineralogical properties.

There is a close link between colour of clay pigments and their mineralogical composition. Therefore aim of this study is to clarify which of the minerals represent clay colour in Upper Devonian clays of Latvia and possible new applications aspects. Study site is Kuprava clay pit in north-eastern part of Latvia where Devonian clays are exposed.

To determine mineral composition, X-ray powder diffraction method was used. Diffractometer X-ray tube operated at 40kV and 30mA, CuKα radiation, diffraction angle range 2° to 70° 2θ and step size 0.050° 2θ. For quantitative analyse data was processed using Quanto software. For granular composition of samples pipette method was used. Colour of all 70 samples was determined using Munsell colour scale, and 26 of them were chosen for detailed study.

Overall there were separated 19 different colour tones, ranging from purple and red tones to greyish. Reddish and gray clays have different mineral composition. Dominating minerals in all samples are illite (30–60%) and quartz (25–40%), in some samples amount of dolomite also is high (till 20%). Elevated amount of hematite and goethite were detected in red coloured samples. Grey and light coloured samples are sandier and there is higher amount of quartz, dolomite and kaolinite than in red samples. Red colouring minerals, like goethite or hematite, are present in all fractions, though amount of hematite, which gives intense red or purple colour tone to the sediments, is much higher in sand fraction, and amount of goethite is higher in clay fraction. Amount of goethite and hematite in red coloured samples is small, approximately 1–5% but such small amounts still is enough to colour clays red.

Results of this study show that colour of clays is mostly dependent on content of iron compounds, and role of other minerals is smaller. Grey clays do not contain ferric compounds, but have high amounts of quartz (35–40%) and dolomite (15–20%).

Results of this study further could be used for research on natural dyestuffs and cosmetics as well as other possible applications.

Acknowledgements: This work has been supported by the European Social Fund within the project „Support for the implementation of doctoral studies at University of Latvia".

Palygorskite clays from Borshhovskoe deposit (Kaluga region, Russia): composition, crystal chemical particularities of clay minerals and colloidal properties

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Palygorskite clays are used in various branches of industry, such as pharmaceutics, constructing, drilling, wine-making etc. Palygorskite clays as a component of drilling fluid are the main application. Clays can form a stable suspension with surplus water. Main technological characteristics of the raw clays are cation-exchange capacity, slurry yield with fixed viscosity etc.

Clays from production horizon of Borshhovskoe clay deposit (Kaluga region, Russia) were used as a test subject. Detailed research which includes study of relation between mineral composition, crystal chemical particularities and colloidal properties of clays should provide better exploitation of deposit and their proper use as a raw material.

The following methods have been used during this study: x-ray diffraction analysis, differential thermal analysis, near-infrared spectroscopy, middle-infrared spectroscopy, grain-size analysis, viscosity measurement (according to API requirements), and measurement of cation-exchange capacity. Characteristics of mineral composition and quantitative mineral analysis were carried out using the data received from XRD-analysis conducted in MSU. Thermal analysis was performed in MSU, infrared spectroscopy was carried out in MSU and Theoretical and Physical Chemistry Institute (Athens, Greece). Technological testing took place in MITHT.

Clays from different areas of upcoming quarry were studied during the research. It was found that clay composition varies from primary palygorskite to montmorillonite clays within the limits of deposit. Montmorillonite has quite stable composition while palygorskite has the complex one. NIR examination results clarified that palygorskite represents mechanical mixture of Al- and Al-Fe-varieties in different proportion with overall prevalence of Al-variety.

Testing the colloidal properties of clay suspensions has demonstrated generally good properties. The application range of these clays is determined chiefly by the quantitative ratio of clay and non-clay minerals, the suspension viscosity and the cation-exchange capacity. Standard technological tests require considerable amounts of time and sample volume. This work will underlie in development of express methods which could be used as fast and precise evaluation of the main characteristics of colloidal properties (used in grade of clay powder analysis) based on mineral composition and particularities of clay minerals structure.

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Mineralogical characterization of talc from the Western Carpathians (preliminary results)

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Several talc deposit are located in Slovak part of the Western Carpathians. The main deposits are evolved in Veporic unit (Early Paleozoic Sinec belt) and in Gemeric unit (Early Paleozoic Gelnica group). Most of talc occurrences in Slovakia belong to the deposits in association with Mg-carbonates [1]. Nowadays, a big talc deposit is opened in Gemerská Poloma. The objective of the study is mineralogical characterization of talc from Gemerská Poloma deposit and his comparison with talc from others areas (e.g. Hnúšta-Mútnik) and also investigation of structural order and crystal size. Research was performed on bulk rock and clay fraction (< 2 μm). Samples were studied by XRD, electron microscopy and IR spectroscopy.

Results from XRD quantitative mineral analysis by RockJock software [2], showed that amounts of talc from Hnúšťa-Mútnik samples vary from 85% to 1%. Samples from Gemerská Poloma contain 90-25% of talc. Other minerals are chlorite, quartz, magnesite, dolomite, biotite, muscovite (illite), and pyrite. The mean thickness of talc crystals from fraction < 2 μm was analysed by BWA technique (MudMaster software, [3]). It was indicated differences in mean thickness of talc crystals. Samples from Gemerská Poloma have bigger mean thickness (23,4 nm) than samples from Hnúšťa-Mútnik (15,6 nm). IR spectroscopy was used for partial crystallochemical characterization of the samples. The specific talc bands were significant in the samples with dominant amount of talc (e.g. OH-stretching band (Mg_3OH) at 3676 cm^{-1} and bending band at 669 cm^{-1}). Presence of small amount of Fe in the talc structure is probably determined by weak stretching band (Mg_2FeOH) at 3660 cm^{-1}. Stretching bands at 3571 and 3428 cm^{-1} were significant in samples with high amount of chlorite. Position of these stretching bands points out the presence of trioctahedral chlorite, probably clinochlore.

Talc samples are composed with platy crystals. Planar surface is almost isometric with dominant dimensions from 3 to 10 μm. The shapes of crystals are anhedral and subhedral according to SEM study.

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Mineralogy of Devonian Timan bauxites

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The mineralogical analysis of fine bauxite ores is recently considered as mandatory component of geological prospects because its results considerably supplement (including nanolevel of mineral formations) concentration techniques and volumes of separated effective mineral and its satellites, quality of mineral raw for further processing of the concentrate.

To evaluate technological characteristics of ore-bearing rocks it is first of all necessary to study in detail various lithotypes of ore-bearing rocks. Therefore we paid special attention to the technique of their material study.

Bauxites are rocks, which components are represented by fine minerals; the study of their mineralogical and physical-technical characteristics allow new look at problems of bauxite concentration.

The most promising new source of this raw in Russia is the Middle Timan group of deposits at the north-east of Komi Republic (reserves up to 200 m depth – more than 200 mln tons). The explored reserves of the Middle Timan are concentrated in the Vezhayu-Vorykva deposit (150 mln. tons).

The deposit includes three types of ores that are different by their lithologic and mineralogic features: hematite-boehmite, hematite-chamosite-boehmite, kaolin-chamosite-boehmite.

The content of boehmite (to 55-65%) often tends to the medium part of the bauxite member. The quantity of silica minerals (kaolin, chamosite and others) increases in top and bottom parts of the section (to 35-45%), but sometimes higher contents of kaolin are determined throughout the whole section.

The features of the mineral composition, as well as the degree of bauxite cementation, affect the degree of substance differentiation, which determines possible ways of concentration. Therefore both, discovery of distribution regularities (in the section or area) of bauxite lithological varieties, and determination of areas of bauxite development with predominance of various minerals, present interest for mapping of areas of concentrated ores development.

During the investigation of the Vezhayu-Vorykva bauxites the characteristic features of mineral composition and physical properties were determined. The high dispersity of the main bulk of composing minerals (mechanical mixtures with micron and sub-micron particle sizes) is characteristic for all the lithologic-mineralogic varieties. For example fine-crystalline boehmite with sizes <5-10 mcm is widely distributed; and also the considerable part of hematite and goethite is concentrated in the thinnest classes (<0.5 mcm). Often isomorphous substitution of iron oxide by aluminum is determined in goethite and hematite with formation of alumohematite and alumogoethite. The main silica minerals are kaolin and chamosite. The major part of chamosite is represented by a fine form; content of iron oxide reaches 10-15%. The X-ray amorhous phase is widely distributed, which is determined at comparison of various diagnostic methods (X-ray structural analysis, chemical analysis, IR spectrometry, Moessbauer spectroscopy).

Characteristics of smectite and palygorskite clays from the Dashkovskoe Industrial Deposit (Serpuchov Region, Russia)

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Palygorskite and bentonite clays are used in many industrial applications. The subject of this research was Dashkovskoe clay deposit (Moscow region, Serpukhov).

XRD analysis showed that samples contain palygorskite, montmorillonite, calcite, dolomite and quartz at various ratios (Fig. 1). Palygorskite is dioctahedral and Al-rich, with very minor FeIII substitution in M2 sites. The chemical composition of palygorskite in the different horizons of the Dashkovskoe deposit is found to be remarkably constant, despite the fact that this mineral is capable to exhibit large variations in the speciation of its octahedral sheet. This indicates that palygorskite was crystallized under the same chemical condition and deposited in sedimentary basin without transportation. Area of Dashkovskoe deposit is represented by a source of palygorskite for Moscow region.

The Dashkovskoe clay suspensions possess quite good structural-mechanical properties. All samples demonstrated pseudoplastic behaviour with Bingham yield value ranging between 1.9 and 9.5 MPa•s (Fig. 1). The best apparent viscosity (AV) and yield point (YP) have been found in the case of nearly 50/50 palygorskite and smectite mixture. This fact can be explained by the presence of optimal quantities of particles with different shapes in dispersion media. It is well known that palygorskite displays good stability in saline solutions and under high temperatures. This is especially important when using drilling mud with rotatory drilling of rocks bearing soluble salts. Thus combining smectite and palygorskite at a certain ratio not only allows acquirement of salt- and thermal-resistant mud but also significantly improves their rheological characteristics.

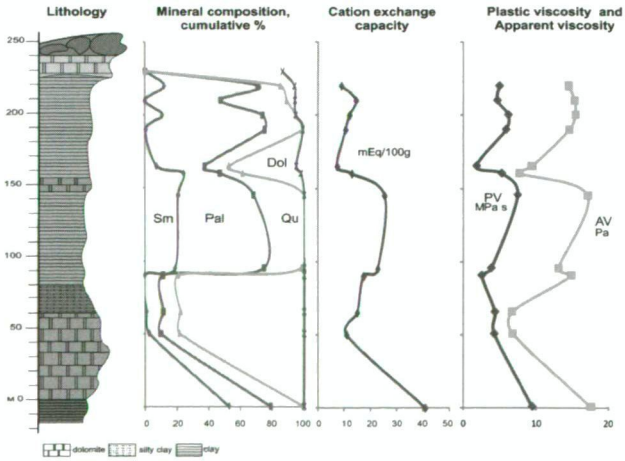

Fig. 1: Relations between lithology, mineral composition, cation exchange capacity and viscosity.

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Identification and stabilization of clays for productivity/injectivity optimization in the hydrocarbon industry

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Most of the sandstone type hydrocarbon bearing formations are severely contaminated by detrital clay minerals, which can cause severe formation damage and productivity impairment. Maximization of productivity of hydrocarbon producing wells or optimization of productivity/injectivity of underground gas storage wells require efficient preferably proactive formation damage control. The most common source of permeability damage in such wells is the destabilization and mobilization of fine particles with fluid flow (fines migration). Clay minerals are mostly prone to disintegration, mobilization and entrapment within the pore structure, causing permanent loss of permeability in case of improper drilling/completion fluid chemistry. In drilling/completion technology design and fluid chemistry optimization the need for characterization and determination of types and concentrations of mineral constituents of formation rocks, especially clay minerals (XRD, FTIR, CEC, etc.) are essential and inevitable and are routinely used to support advanced field practice.

Fluid flow in the porous formation is controlled at pore scale, while fines migration at micron-to-submicron scale, therefore extensive studies of pore structure/morphology and visualization, identification of potentially mobilizable particles and their typical position in the pore structure (SEM, ESEM) are also key issues in combating permeability reduction. Clay minerals commonly appear in a very complex coexistence with different detrital minerals.

Core flow studies (using representative core plugs) can efficiently support to evaluate the potential fluid chemistry/flow effects at semi-macro scale, but can't give direct answer for the effect of formation heterogeneity.

Potassium salts and selected cationic (organic) polymers of different molecular weight and other specialty additives are the key components of the new "fit-to-purpose" drill-in and completion fluids, which were formulated by complex engineering approaches. The main tasks in Hungary are to maintain formation integrity and to control formation damage in mostly under-consolidated, water-sensitive sandstone reservoirs.

The paper gives an overview of clay identification and stabilization techniques, results and illustrates their aspects in drilling/completion fluid design and successful field applications.

Evolution of boron and nitrogen content during illitization of bentonites

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The contents of boron and nitrogen in illite-smectite clays from pyroclastic horizons of sedimentary rocks (bentonites) were studied using samples from different sedimentary basins, representing a complete range of diagenetic alteration. Bentonites were chosen to deal only with the authigenic clay, avoiding complications related to the recycled (detrital) clay material. The bulk rock chemical measurements, performed on raw rock samples in order to avoid any loss of exchangeable B and N, were referred to the contents of illite-smectite clays and to the content of illite alone, both measured by a combination of XRD and chemistry-based techniques [1].

The results indicate that the smectite illitization reaction in the studied range between 100 and <20 %S is not so much redistributing B and N present in the original smectite, but it is a net consumer of both boron and nitrogen from the pore waters.

Both B and N (as NH_4^+) are contained mainly in illite, so their contents in illite-smectite clay increase in more or less linear manner with progressing illitization. The content of N in illite layer is decreasing during diagenesis and the content of B is either decreasing or remains stable. In one diagenetic cycle bentonitic illite fixes up to 800-1000 ppm B and up to over 1% $(NH_4)_2O$, corresponding to over 20% of the fixed cation sites.

The studied rocks are different from regular sedimentary clays, because smectite in bentonitic horizons is not detrital but it crystallizes *in situ* during early diagenesis at the expense of volcanic glass. The conclusions drawn above refer only to this particular case. Similarities in diagenetic evolution of boron and nitrogen contents of illite, documented in this study, argue in favor of the kerogen as the dominant common source of both elements in sedimentary basins.

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Reservoir properties dependence upon the compositional features of clay minerals

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Present-day core laboratories widely use the following method of clay content evaluation. The term "shaliness" is considered as an ability of rocks to contain particles with diameters d<0,01 mm, in the US laboratory practice d<0,001 mm. Hence, clay content is estimated by means of sieve analysis procedure.

Nevertheless, described approach eliminates the probability of fine-grained oxides and hydroxides of silicon and aluminum which aren't related to clay minerals. Besides, clay fraction can be underestimated as the diameter of large kaolinite crystals exceeds 0,01 mm. Providing clay content is calculated thus-and-so, mistakes in formation evaluation are expectable.

Presence of certain clay minerals can indicate particular sedimentation conditions. Analyzing the alteration of clay minerals composition, it is possible to define depositional environments more exactly.

There is close correlation between depositional environments and natural radionuclide distribution. This fact is a basis for applying spectral gamma ray in order to determine clay mineral composition. Also, it is very helpful to estimate clay minerals content quantitatively using X-ray analysis, infrared spectroscopy or thermal gravimetric analysis.

Clay minerals impact on properties of oil and gas reservoir in a significant way. The study of clay minerals composition and estimation of their influence on physical and fluid-flow properties of rocks is a vital and high-demand task.

Clay minerals belonging to various groups affect reservoir properties differently. The estimation of a pore space filled by a clay material and the influence of certain clay minerals on filtration properties is applicable to drilling technology, formation evaluation and oilfield development. The information about clay minerals composition is used for adjustment of log-derived evaluation algorithms.

In the research the in-depth analysis of clay minerals is presented in scope of their effect on petrophysical properties of rocks. Also, the application of infrared spectroscopy for a qualitative and semi-quantitative estimation of clay minerals content is addressed.

Multi-constituent modeling of gasoline contamination in laboratory – sorption of light hydrocarbons by clay

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Petroleum hydrocarbons are common site contaminants, but little is known about their natural attenuation processes. Due to the diversity of hydrocarbon compounds a range of remediation technologies may be applicable. Volatilization and gas transport of VOCs are the bases for some remediation technologies (for example soil venting, air sparging, and soil vapor extraction), consequently knowledge of the volatility of hydrocarbon compounds is important for understanding their fate in subsurface media. In order to investigate volatility and sorption of light hydrocarbon compounds, a special column experiment was conducted in laboratory.

The volatile components of the used hydrocarbon could be transported only in one direction (upward through fillings), therefore the investigation of their sorption on natural clay and sand was possible. At the end of the experiment more than half of the initial fluid volatilized, due to the volatility of the individual constituents. The volatilization was very effective in the first year.

The sorbed HCs are mainly paraffins and aromatics, while napthenes rarely occur. After half a year, n-C_7 was found to be the lightest and C_{11} the heaviest constituent. The range enlarged continuously, it was possible to measure n-C_6 and C_{12} after one year, while at the end of the modeling n-C_5 and C_{15} were already measurable in clays. It was possible to detect sorbed HCs after half a year only in clay layers and in every sample at the end of modeling. Quantity of sorbed compounds decreased with growing carbon numbers. Models with clay-caps contained larger amounts of HCs also in deeper layers compared to their sandy pairs (totally three to six times more quantities). The reason for this is presumably the good sealing property of the clay, therefore volatilized components remained in the pores among sand particles or sorbed onto the individual constituents. Quantity of sorbed HCs is the greatest in the vicinity of the fluid phase. Fine tendencies, dependent on depth, can be seen mostly in case of cyclohexane, benzene, as well components with slightly larger carbon number (e.g. C_{10}, C_{11}, C_{12} and C_{13}). These clearly show the effect of less volatility.

By comparing the results of detailed analyses (GC, Rock-Eval, XRD), adsorption was the main sorption process.

On the basis of comparative assessment of the results derived from the analyses of samples from different phases (fluid, gas and solid), the best practice for identifying the source of a gasoline type contamination is a joint analysis of sorbed and free hydrocarbons of the soil samples, while the best way to monitor a contamination is to analyze free gas components. It is worth applying the analyses together, because a different range of the initial fluid phase can be measured from the free gas and the sorbed phase. The ratio of the lightest hydrocarbons in the total amount of hydrocarbons may indicate the time when the contamination occurred.

Laboratory methods in evaluation of shale interaction with drilling fluids: effect of clay content and shale characterization

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The behavior of shale samples exposed to drilling fluids may differ significantly due to the rock characteristics. Type and amount of clay minerals, rock structure, distribution of minerals, and other geologic features are important elements that need to be integrated in the execution of successful testing programs. This paper includes the descriptions of different test methods used to evaluate the interaction between shale and drilling fluids and how the characteristics of the shale samples are used to select the experimental methods. Understanding and comprehending clay content and distribution in the shale samples is one of the most valuable steps before the testing. The response of clays with fluids can be manifested in swelling process, dispersion, propagation of fractures and other mechanisms. The type of response can be closely related to the type of clay. The rock structure and mineral distribution also play important roles. Presence of laminations, lenses, and just bulk structure may control, restrict or direct the areas where the fluids can interact with the clays in the rock. Compositional and structural variations in shale samples can be obtained from shale samples and constitute the base information for the selection of the laboratory tests for the drilling fluid design.

Clay minerals features application for reservoir pressure estimation

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This research is devoted to the development of the abnormally high formation pressure (AHFP) zones determining innovative technique on well logging data. The method is based on changes in dependences of clays physical properties in AHFP zones. It takes into account the nonsteady thermal field in the borehole.

Normal pressure is formation pressure is due to the presence of fluids in pore spaces of the rock matrix. Abnormal pressure is any geopressure that is different from the established normal trend for the given area and depth.

AHFP represent a serious threat for the well and its staff maintenance while deep wells drilling and development. High technological and economic performance in drilling and deep wells development can be achieved in case of correct prediction and estimation of AHFP zones.

Abnormal pressure predicting methods in the thickness of sedimentary rocks are based on the pattern of rocks properties changes as a result of compaction in the process of sediments accumulation. Physical properties of pure clays, used as an indicator of pore pressure, are determined by its compaction degree. Clayed rocks containing deposits with AHFP are less sealed and have higher porosity in comparison with similar rocks with normal pore pressure [1].

Physical parameters depend on rocks density and as result porosity. This dependence of clayey rocks is the basis of various identifying and estimation by abnormal pressures methods.

There are following methods for AHFP zones predicting: equivalent depths method, «normally clay compacted curves» technique, compression curve method.

Factors determining changes in physical properties of pure clay rocks are changes of clay mineral composition and temperature. However, the impact of changes in clay mineral composition at depths of more than 2000-2500 m (in AHFP zones) is nonessential fact. A significant contribution to the calculation of reservoir pressure makes temperature [2].

Temperature correction is traditionally calculated on the geothermal gradient. Nevertheless, the real thermal field in the borehole can differ greatly from stationary geothermic data. Therefore, thermal field in the borehole was simulated. Also the distribution of the temperature over time after flushing out of well was surveyed within the radius of well logging methods study.

Authors investigate the thermal field formation in the vicinity of the borehole. Dynamics of the thermal field during drilling, well cleanout and well shutdown are studied. Temperature factor effects on the accuracy of abnormal pressure on well logging data calculation are determined. A modified «normally clay compacted curves» technique is developed. It involves the introduction of the correct temperature adjustment to electrologging curves before the line of normal clay compaction tracing.

Formation of thermal field in the vicinity of the borehole was investigated. Innovative method AHFP calculation, based on changes in dependences of clay physical properties in AHFP zones and taking into account nonsteady thermal field in the vicinity of the borehole, was developed. Maps of abnormal pressures and anomaly pressure coefficients in sediments of Bazhenov formation were charted.

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Possibilities of gamma-ray log quantitative interpretation

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Current work is devoted to studying of influence of separate clay minerals on collector properties and to definition of their maintenances according to gamma-ray log in complex of well-logging data.

On the basis of the revealed laws, petrophysical modeling of collectors and adaptive techniques of well-logging data interpretation [1] the algorithm of an estimation of kaolinite and hydromicas maintenances in structure of clay cement was developed (Fig. 1). In this work results of interpretation of Jurassic deposits of Tevlinsko-Russkinskoe field (West Siberia, Russia) are presented.

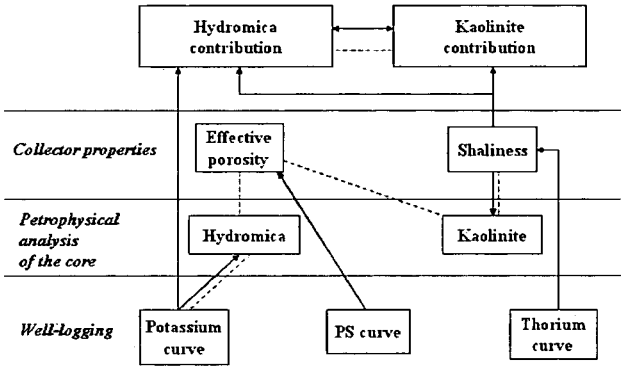

Fig. 1: The scheme of estimation of kaolinite and hydromica maintenances in cement of terrigenic collectors.

The ways of an estimation of kaolinite and hydromica maintenances in clay cement of collectors according to gamma spectrometry in complex of borehole surveys are offered. It's based on their interrelation in clay cement of terrigenic collectors.

It is revealed that character of ratio between contributions of hydromica and kaolinite in clay cement of terrigenic collectors is maintained for different adjournment of various deposits.

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The specificity of clay minerals influence on the residual water layer formation

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Clay minerals have specific features. A distinctive feature of all clay minerals is their high dispersity. High dispersion creates a well-developed specific surface area of rock (up to 800 m2/g for montmorillonite), which causes a high margin of free surface energy and the manifestation of molecular interaction forces in the surface layers. The most important physical-chemical characteristics of clay minerals is their ability to surface dissociation (formation of a water shell), the ability to anomalous high ion exchange (cation exchange capacity) [1]. Patterns of distribution of residual water saturation for the multimineral reservoirs are complex and nonlinear. Dispersion of clay material greatly affects the quantitative assessment, and even small admixture of chlorite or hydromica will make significant changes.

Appearance of reservoir nonuniformity on the dependence of residual water saturation from the total porosity due to clay minerals variation is discussed. The set of factors contributing to the heterogeneity of the matrix and cement composition and properties, defines the dynamic range of cement and matrix properties, which is why scatter points on the plane residual water saturation – total porosity appear. This means that, although the dependence between residual water saturation and total porosity, as well as other petrophysical relations, the "statistical" comparisons is not functional, but it is not in the full sense of statistics. The scatter of points in the field of correlation is due not only to measurement errors, but to the differences in petrophysical properties of clay minerals comprising the matrix and cement. Petrophysical informative field configuration have the degree of correlation and the scatter of points in the field of correlation. The most general definition of a complex manifold, regardless of the nature of the latter, will be the following: complex reservoirs are reservoirs, which are meaningless concepts conditioned values of petrophysical characteristics, or relevant testimony well logging techniques.

Filtration, capacity, and structure, water storage capacity and other petrophysical characteristics depend primarily on the content of clay minerals, their composition and morphology in terrigenous reservoirs. If no or little content in the carbonate rocks, silicate and iron cement quantity and composition of the clay material is a decisive factor in the separation of rocks on the reservoirs and non-reservoirs.

In conclusion, for reservoirs with multimineral composition, the dependence of residual water saturation from total porosity cannot be unambiguously determined. For each part of the reservoir, this dependence can vary, due to the heterogeneity of the mineral composition.

All types of reservoirs and their filtration-capacitive properties manifested in different kinds of dependencies residual water saturation – total porosity. With a fixed capacitance matrix of the diversity of these relationships is due to a variation of the properties of clay cement.

This heterogeneity of polymineral clay and other reservoirs can formulate, the most common definition of "complex" reservoirs, as such, which make no sense notion of fixed values conditioned volumetric or appropriate evidence of well logging techniques.

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Burial diagenetic processes of clay mineral and non-clay mineral, and their relation to quartz cementation in sandstones of the Siri Canyon, Danish North Sea

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The deep marine sandstones in the Siri Canyon, Danish North Sea, have been reported to import significant amounts of dissolve silica from adjacent Palaeocene shales during early diagenesis, and the authigenesis of silica developed several morphologies in the studied sandstones. We have studied the diagenesis of one of these shales, the Sele Formation shale, to document the diagenetic steps which release silica and to evaluate the possible capacity and timing of silica export from the shale into the interbedded sandstones. Initially, the shales were rich in smectite and had variable admixtures of silicious fossils (diatoms, radiolarian and sponge spicules) and volcanic ash.

Depth dependant alteration of the various components in the shale, results in successive stages of silica-release. In shallow samples (<1700 m), the alteration of volcanic ash has already been completed. Released silica was partly consumed for the precipitation of smectite and zeolite. Opal-CT is not systematically related to volcanic ash, and some silica may have been mobilized and migrated into the interbeded sandstones. In addition, a major part of the biogenic silica has been transformed into opal-CT and partly to microcrystalline quartz. The microcrystalline quartz is an internal sink for dissolved silica, but the shale may also have been an active silica exporter during this transition.

With deeper burial (2000-2900m), opal-CT is fully transformed to microcrystalline quartz. During this phase, silica has been partly mobile and depending on the rate of dissolution compared to the rate of precipitation, silica may have been lost to sandstone cementation. Zeolite is also dissolved and mobilized silica may also have activated the shale as silica exporter.

At deep burial, iron-rich chlorite has replaced a minor part of smectite. The smectite to chlorite transformation released silica at the expense of iron. Therefore, a third phase of silica mobility was active. Microcrystalline quartz may have been an internal sink, but the shale would also be a potential silica supplier at this stage. At maximum burial depth (2900 m), the major part of the smectite is still not transformed, and the smectite to illite transformation has not yet been activated as a potential silica source. Early cementation by opal and microquartz depends on the supply of dissolved silica from a readily dissolvable source. The process starts with biogenic silica dissolution and supersaturation of pore fluids with respect to opal-CT and quartz. Relative rates of opal-A dissolution and opal-CT nucleation govern the extent to which silica activity is buffered and hence the possible silica flux into adjacent sandstones. With progressively less remaining opal-A, silica activity starts to decline and opal-CT nucleation becomes subordinate to growth. Precipitation of cryptocrystalline quartz began once the thermodynamic drive for the opal-CT became insignificant. Relative rates of opal-CT dissolution with respect to quartz nucleation and growth buffer the silica activity and the possible silica flux into adjacent sandstones. The early stages of the sandstone diagenesis are dominated by massive precipitation of opal cement and microquartz. This indicates a large flux of silica at the time of opal-A to opal-CT transformation and possibly at the time opal-CT to microquartz transformation. Therefore, the dissolution rate of precursor phases (biogenic silica, opal-A and/-CT) was fast enough to create a sufficient silica gradient to exports silica from shale to sandstone.

Molecular simulation of the hydration of methane confined in the clay interlayer or in nanopores between clay basal surfaces

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Methane hydrate is not only a potential energy resource, but also would be an ideal crystalline solid for gas storage. In general, the rate of nucleation and growth of the clathrate can be increased by operating at either higher pressure or lower temperatures, but such conditions may be undesirable for many applications. One of the alternative strategies to increase the kinetics of clathrate formation is to increase the interfacial contact between liquid water and the gas by inducing solid supports such as silica [1] to generate a thin, confined water layer in contact with the gas. The promotion mechanism of the clathrate nucleation and growth by mineral surface should be disclosed in order to understand the formation of methane hydrate in muddy sediments and in artifical conditions. In this study, molecular dynamic simulations have been carried out to investigate the formation and stability of methane hydrate in Na-smectite interlayer with different layer-charge distribution and water content, as well as in the nanopores with clay walls in various P-T conditions. In the simulation, the MD program Dlpoly and Clayff forece field [2] was employed.

The simulation results indicate that the methane clathrate can be formed in the interlay spaces under much higher temperature and lower pressure than that of the bulk hydrate. As methane molecules confined in the interlayer of clay minerals, most of the methane molecules are solvated by nearly 12-13 water molecules and coordinated with six oxygen atoms from the clay surface simultaneously. The methane molecules are generally trapped in the six-member rings through the strong H-bonds, which is exactly similar to the behaviors of K^+ or Cs^+ in montmorillonite interlayers [3]. The self-diffusion coefficients of the methanes in the newly-formed cages remarkably decrease from 0.452×10^{-9} m^2/s to 0.060×10^{-9} m^2/s at 277 K and 50 atm.

The layer-charge distribution displays remarkable effects on the stability of interlays hydrated methane complexes. A clay surface with negative charge sites is hydrophilic and present lowers surface affinity for methane moleculars. As the net layer charge is similar, the distance between negative charge sites and methane moleculars play important roles. It is disclosed that the tetrahedral negative charge site near the surface is hydrophilic and reduces the clay surface affinity for methane, which leads to less stability of hydrated methane complex in the smectite with tetrahedral substitutions. As Arizona-type montmorillonite has no tetrahedral negative charge site, the hydrated methane complex in it is more stable than other clays with tetrahedral charges.

The stability of the methane hydrates confined in nanopores with talc basal surface also shift to the higher pressure region depending on pore size when compared with those of bulk hydrates. The surface of the clay walls act as templates for the cystallization of methane hydrate, and a layer of methane hydrates are firstly formed, which is tightly contacting to the clay surface.

Acknowledgements: Authors acknowledge National Science Foundation of China (No. 40973029).

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Increase of porosity in turbiditic sandstones by late-stage diagenetic formation of chlorite and kaolinite

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Core material of miocene aged turbiditic sandstones, located in the Nile Delta area (Egypt), have been analyzed by means of thin-section petrography, scanning electron microscopy/ energy dispersive X-ray, petrophysical measurements, X-ray diffraction and IR-spectroscopy.

The sandstones vary from fine grained- to conglomeratic sandstones, representing ancient channel fill deposits. Values of porosity range from 2-32 % and permeability vary between 0.005 and 1100 mD. Eodiagenetic alterations are represented by moderate mechanical compaction and grain reorientation, calcite replacement of former aragonitic clasts and formation of anatase, siderite and pyrite. Early quartz precipitation occurs as quartz overgrowth. Mesodiagenetic alterations are mainly represented by illitization of smectites, quartz overgrowth, formation of chlorite and kaolinite and late-stage pore filling calcite.

Evolution of the reservoir quality has been controlled by both, eodiagenetic and mesodiagenetic processes, and shows that formation of secondary porosity plays an important role. Whereas primary porosity occurs mainly as intercrystalline macroporosity and takes 30 Vol.-% of total amount of porosity, secondary porosity comprises around 70 Vol.-% of total amount. The main part of secondary porosity belongs to intercrystalline micropores between chlorite and kaolinite. Investigations indicate that the formation of chlorite and also kaolinite proceeded at a late stage of diagenetic history, later than generally expected. It occurred via transformation of Fe-Mg rich detrital grains, fragments and clayey compound as well as precipitation within open pore space. This "late-stage formation" might be the result of rapid burial to greater depths and therefore decelerated mineral reactions. Thereby the detrital components stabilized the framework to a certain degree and prevented the sediment for strong mechanical compaction prior to the formation of chlorite and kaolinite. Thus, the new formed intercrystalline micropores increase the total porosity and also permeability of the reservoir section.

Mineral stability of bentonites as potential barriers

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Bentonites are widely tested and used as a barrier material, due to their exceptional properties like plasticity, very low hydraulic conductivity, expandability and cation retardation capacity. All these parameters are directly related to the smectite - bentonite's the most important mineral component. That is why its properties are so important, particularly if a very long-term stability is required (e.g. radioactive waste repositories).

In this study a variety of possible impacts on the smectite structure were tested focusing mostly on the material from two large Slovak bentonite deposits (Jelsovy Potok, Lieskovec). The Jelsovy Potok represents Al-Mg bentonite and the Lieskovec belongs to Fe-bentonite. Several additional well known bentonites were used for some specific comparative tests. Particular attention was focused on the effect of temperature, impact of the acid and the alkaline solutions, and the gamma radiation. A special attention was focused on the bentonite-iron interactions. Iron used in the study was in the form of a 99 % pure Fe^0 powder metal, as well as in the form of pyrite and Fe oxyhydroxide. Pure metal should represent the possible iron construction elements of the repository. The pyrite and the Fe-oxyhydroxide should represent the iron sources from the geological environment of the repository. The batch laboratory experiments, as well as the long-term mock-up test, on the compacted bentonite blocks, were used.

Several laboratory techniques were used to test the reaction products including the XRD, FTIR, UV-VIS, AAS, electron microscopy of the ultrathin sections etc. Basically a large stability of bentonites towards the acidity and the alkalinity at the moderate conditions was confirmed. The smectites lost their original properties only if the extensive treatments in the batch experiments were applied.

No effect of heavy doses (up to 1,5 MGy) of gamma-radiation on the structural and mineralogical parameters (crystal size distribution, specific surface area, cation exchange capacity, layer charge, etc.) of the smectites was identified. Equally no effect was observed during the interactions with the iron in the form of pyrite an/or Fe-oxyhydroxide. Neither batch nor the mock-up tests revealed the changes of the smectites.

Different situation was observed during the interactions of bentonites with a pure iron. The batch experiments showed the significant changes – formation of the magnetite and 7 Å phyllosilicate (berthierine-like), dissolution of the silica phases and deterioration of the smectite structure. Fe-rich smectites were affected more than the others. Mock-up tests with the iron did not show any impact on the bentonites.

Overall we can confirm a long term stability of the bentonites from both deposits at the moderate pH conditions (pH 4-8), resistance towards gamma radiation, and no interaction with the iron. Only potential risk could be linked to the Lieskovec Fe-bentonite extreme exposure to the interactions with pure Fe.

Seeking relations between metal fractions and clay mineralogy in the urban soils of Lisbon city (Portugal)

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This study is a part of the working program of a research project untitled "PTDC/CTE-GEX/68523/2006: URBSOIL-LISBON_ Geochemical survey of Lisbon urban soils: a baseline for future human health studies". The aim of this research is to assess the control exert by soil clay mineralogy in the fixation of contaminants in the urban soils of Lisbon city, Portugal. To achieve this aim, the specific bonding forms of heavy metals (Cu, Zn, Pb, Ni and Co) to the clay minerals of several soil phases of Lisbon urban soils will be determined. A total of 51 soil samples were collected over Lisbon city. Figure 1 shows the sample sites and classed post map of the % of clay. Each sample site is labelled from 1 to 51. Thirteen samples were selected based on the percentage of the clay fraction in each sample.

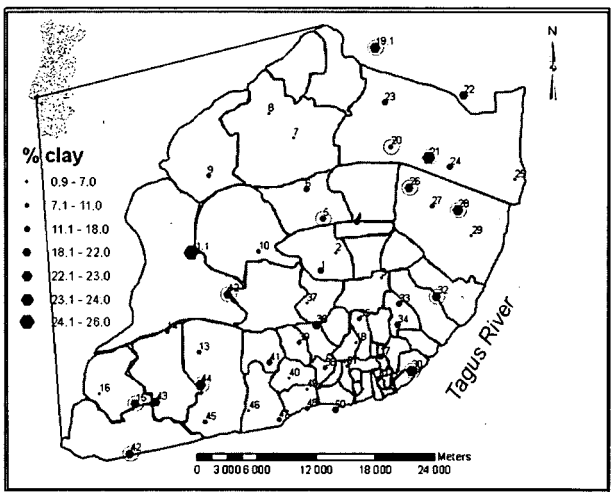

Fig. 1: Soil sampling sites and classed post map of the % of clay fraction; the circles identify the samples used in this study.

The results show that the clay minerals play different roles for the different metals in the soils. High concentrations of Co and Ni occur in samples with high contents in esmectite and low or null contents of illite. The role played by clay minerals in the fixation of Pb, Cu and Zn in the studied soils is still not clear, needing more research. Most of the Pb in these urban soils has an anthropogenic origin being present essentially in the extractable cation soil phase. Like Pb, Cu and Zn have also essentially an anthropogenic origin. The results suggest that organic matter plays an important role in the fixation of Cu while carbonates seem to be effective restraining the mobility of Zn.

Photosensitizer/clay mineral colloids as potential disinfection materials

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Methylene blue (MB) adsorbed on clay mineral surface forms molecular aggregates [1] and looses its photochemical (photosensitizer) activity [2]. Whereby MB dilute aqueous solutions produce large amounts of singlet oxygen ($^1O_2$), its production was significantly reduced in MB-clay colloids. The photoactivity of MB solution and hybrid MB/clay colloids was measured directly by luminescence measurements at near infrared region and by electron spin resonance spectroscopy (spin-trapping method).

Surprisingly, enhanced antimicrobial effects of MB were achieved in the colloids of montmorillonite. Under visible light irradiation, MB/montmorillonite dispersions prevented the sporulation of *Aspergillus niger* and *Penicillium* sp.

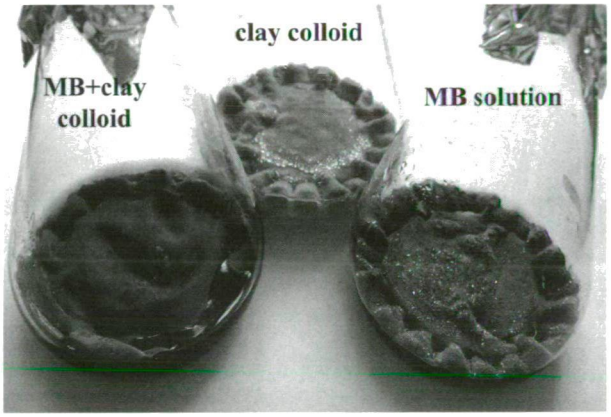

Fig. 1: Reduction of *Aspergilus* sporulation in methylene blue/montmorillonite colloid. No spurulation was observed in the dye/montmorillonite colloid. Sporulation was influenced neither in clay colloid without the dye (middle) nor in MB solution (right).

Moreover, the presence of clay mineral colloidal particles inhibited the growth of yeasts *Candida albicans* and bacteria *Escherichia coli*. *Staphylococcus aureus* proved to be the most susceptible to the MB/clay effects and its growth was significantly reduced even at the lowest dye concentrations ($1.1 \cdot 10^{-6}$ mol dm^{-3}).

The contradiction between enhanced antimicrobial properties and reduced $^1O_2$ formation in MB/clay colloids can be explained in terms of the mechanism of antimicrobial effect. The role of clay particles is most likely to promote the contact between the surface of microorganism cells and MB cations. Clay particles mediate the delivery of dye molecules on the surface or inside the cells. Dye solutions, although producing large amounts of $^1O_2$, were inefficient against microbes, because of a short lifetime of activated oxygen species. The enhanced activity of photosensitizers in clay colloids indicates new perspectives of the implementation of clay minerals in environmental industries for microbial disinfection [2].

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Effect of particle preparation on intercalation of vermiculite using HDTMA cations

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Vermiculite has a significant commercial and technological importance. It is 2:1 planar hydrous phyllosilicate that can be modified using intercalation by various organic cations in the interlayer space similarly as smectites. This modification makes possible among others to use an organovermiculite as sorbent for nonpolar organic compounds from polluted water or gas in the environmental technologies. Organophylic vermiculites were prepared by using hexadecyltrimethylammonium and hexadecylpyridinium cations with various organic cation loadings and their effective sorption ability for non polar organic compounds from water and gas phase was studied [1,2].

Vermiculite particles were prepared for intercalation using two procedures: 1) Conventional sedimentation. Particle size fractions < 5 and < 2 μm were obtained (according to Stoke's law) and 2) Jet milling. Three different fractions under different conditions characterized with particle size < 5 μm. Particle size distribution and specific surface area were measured. Morphology of vermiculite particles was studied using SEM and AFM. It was found that morphology of particles after sedimentation did not change. Particles after jet milling had corrugated edges. This characteristic can contribute to the effective accessibility for organic cations between layers. The effectivity and intercalation rate of the synthesized vermiculite/hexadecyltrimethylammonium intercalates were determined based on the content of organic carbon and characteristics from IR spectrometry and XRD analysis. The results confirmed that intercalation rate of vermiculite size fraction prepared using sedimentation procedure was distinct from intercalation rate of those size fraction obtained using sedimentated and jet milling.

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Effect of wetting and drying on metal-adsorbed montmorilonites

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It is well known that several subsequent wetting and drying (WD) causes the "illitization" of potassium saturated montmorillonite, and thus the loss of expansion and adsorption capacity of the original clay mineral. In this work heavy metal adsorbed (Cu, Pb, Zn, Cd, Co) montmorillonites with different layer charge were submitted to WD cycles. The aim of this study is to reveal the effect of WD on the mineralogical properties of montmorillonites by means of X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

Decrease of the intensity and broadening of 001 peak are general features on the XRD patterns for all metal-adsorbed montmorillonites indicating the decrease of the crystallite thickness with WD cycles (Fig. 1).

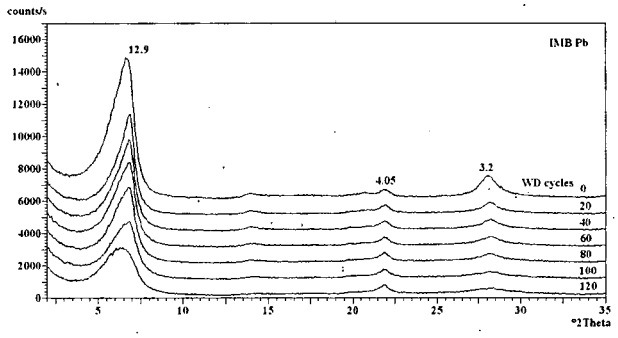

Fig. 1: X-ray patterns of Pb-adsorbed montmorillonite submitted to WD cycles.

TEM analyses revealed the significant decrease of the particle size and the thickness of montmorillonite grains. After 120 WD cycles one or two layer thick crystallites are not rare, and the lateral dimension does not exceed 20 nm. This decomposition due to WD is influenced by the number of WD cycles and by the nature of the metal ion. Pb-montmorillonites are the best affected, because Pb is fixed in the montmorillonite structure and becomes partially non-exchangeable. Chemical composition of montmorillonites also changes with the number of WD cycles, the heavy metal and Si content increase. A possible way of Contrary to K-montmorillonites, metal adsorbed montmorillonites do not lose their expansion capacity during WD. Mineralogical and physico-chemical changes due to WD have relevant application importance, for example in the characterization of the clay liners of waste deposits.

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Photocatalytic degradation of anionic dye by Zn-substituting layered double hydroxide in water

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Photocatalytic reactions are currently attracting a lot of attention as an efficient and sustainable purification procedure in water contamination. In photocatalytic reactions, degradations of some chemical substances are induced after an approaching or adsorption on the surfaces of photoactive materials. However, major photocatalysts such as TiO_2, ZnO and CdS show little adsorption performance for ions. On the other hand, layered double hydroxide (LDH) has extremely high anion adsorption capacities, and these are well known as anionic clays. Recently LDH has received considerable attention as environmentally-friendly materials because of its harmless composition. It is also noted that LDH has catalytic and photocatalytic properties associated with its solid basicity or modifications with various polyacids. However, the photocatalytic properties of LDH itself have not yet been fully elucidated. There are a few studies [1, 2] of photocatalytic behaviors of LDH for organic substances, but the actual photocatalytic function of raw LDH was not clearly marked in these previous studies. To examine the photocatalytic activity of non-treated LDH itself, this study focused on the photodegradation of anionic dye by synthetic Zn-Al LDH in aqueous solution under light irradiation. It is particularly expected that Zn-substituting LDH has a potentially photocatalytic activity since ZnO exhibits a remarkable photocatalytic ability.

Photocatalytic degradation of anionic dye, sulforhodamine B (SRB), was determined along the following method. SRB aqueous solution of 0.01 mmol/L was mixed with synthesized Zn-Al LDH in polypropylene centrifuge tube. The solid concentration was adjusted at 50 mg/L. The suspension was dispersed in an ultrasonic bath, and then placed in a shaker for 24 hours at room temperature. It was conducted under light shielding. The suspension was added in a quartz cell, and served to light irradiation experiments using a super-high pressure mercury lamp (250 W) or a xenon short-arc lamp (500 W). The absorbance of SRB was monitored with an UV-Vis spectrometer during light irradiation.

The absorption band of SRB was appeared from 450 to 620 nm, and SRB presented absorption peak at 565 nm. The absorbance of SRB with Zn-Al LDH was unchanged after leaving in a dark condition. The result suggests that Zn-Al LDH itself didn't have just a catalytic activity. On the other hand, it was observed that the absorbance of SRB with Zn-Al LDH gradually decreased during light irradiation. The degradation rate of SRB with Zn-Al LDH was reached approximately 50 % in 300 minutes of mercury lamp irradiation. After xenon lamp irradiation, more than 50 % of the initial SRB with Zn-Al LDH was decomposed within 60 minutes. And degradation rate of SRB with Zn-Al LDH was faster than in SRB without LDH during both lamps irradiation. Therefore, Zn-Al LDH certainly has the photocatalytic activity for SRB, and the degradation and decolorization reactions are accelerated without being stabilized under UV irradiation. It was expected that Zn-Al LDH could be utilized as an efficient photocatalyst for harmful organic anions.

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Clay biopolymers matrix (montmorillonite modified by biofilms) to improve uranium uptake: adsorption isotherms models

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Uranium is heavy metal, with noticeable toxicity associated with nuclear energy processes and acidic mine drainage. Conventional sorption techniques for heavy metals removal from wastewaters are not useful due to the great volumes treated and the low concentration of pollutants.

Biosorption is an alternative process where different types of biomass allow concentrating heavy metals from diluted solutions. Among the biomass described until now bacteria, algae and fungi were the most used.

Fungal biomass had the advantage of being easily and low cost generated. The main technological drawback in biosorption processes is getting a suitable immobilisation of the biomass to obtain efficient biofilters. A methodology to increase biosorption surface and retain biomass is to generate clay biopolymers matrix. Montmorillonite (MMT) clays have optimal characteristics to be used as innocuous sorbents, with the advantage to be able also to complex all kind of organic as well as inorganic compounds on its surface.

In this study, two fungi: *Aphanocladium* sp., *Acremonium* sp., and the acidophilic bacteria *Acidithiobacillus ferrooxidans* were used as microorganisms growth supported on MMT matrix (in P5 and K9 saline media, respectively). The Uranium adsorption isotherms on all MMT/biofilm studied were fitted to Langmuir, Freundlich, Tempkin, Redlich-Peterson, and Toth models, in order to determine monolayer coverage of adsorbate over homogeneous adsorbent surface; heterogeneous system; indirect adsorbate/adsorbate interactions; homogeneous/heterogeneous system and systems with submonolayer coverage, respectively.

MMT/microorganisms systems were characterized by specific surface area determined by water vapour adsorption (Sw). Also, XRD (analysis of the reflection peak d(001)) was applied on MMT/microorganisms systems and Uranium adsorbed on MMT/microorganisms systems.

Specific surface area (Sw) indicates differences from -5% to +50% for MMT in P5 and K9 saline media, respectively. While the different microorganisms growth on MMT evidenced only around 5-10% difference respect to the Sw value of MMT.

All MMT/microorganisms systems showed higher maximum Uranium adsorption that those obtained from microorganisms or MMT alone.

Adsorption isotherms for MMT+ *Aphanocladium* sp fitted with Freundlich model while MMT+ *Acremonium* sp. and MMT+ *Acidithiobacillus ferrooxidans* fitted with Toth adsorption model, indicating the presence of heterogenous and submonolayer coverage, respectively.

The XRD analysis of the reflection peak d(001) performed on MMT and MMT/micro organisms indicated: intensity decrease and interlayer space collapse with the microorganisms presence respect of that of raw MMT. This behaviour was mainly produced by the different saline growth media or an interlayer water displacement by the microorganism entrance in the interlayer space.

Uranium adsorption shift the MMT reflection peak d(001) around 3.5Å, indicating an Uranium entrance in the interlayer clay space.

Comparison of the physicochemical and catalytic properties of micro- and mesoporous Fe-containing materials in phenol oxidation

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Nowadays, the increasing water utilization in industrial and agricultural activities leads to the expansion of wastewater containing pollutants, such as phenol, which is of the main chemical pollutants. Fenton type homogeneous catalytic systems ($Fe^{2+}/Fe^{3+}/H_2O_2$) are known active catalysts of PhOH complete oxidation with H_2O_2. Iron-containing solid materials have attracted considerable attention as heterogeneous replacement of homogeneous systems due to their Fenton like behaviour. We review herein major aspects of our research in this field for iron-containing high-surface-area pillared clays (Fe-PILC and Fe,Al-PILC) and iron-containing mesoporous molecular sieves (Fe-MMM and Fe,Al-MMM). Fe-PILCs and Fe,Al-PILCs were prepared from naturally occurring montmorillonites by exchanging interlayer ions to Fe^{3+} and Keggin type cation $[FeAl_{12}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ($FeAl_{12}^{7+}$), correspondingly [1]. Fe-MMM and Fe,Al-MMM were synthesized via sol-mesophase rout under weak acidic conditions using Fe^{3+} and $FeAl_{12}^{7+}$ as Fe and Al source, correspondingly [2]. XRD, low-temperature N_2 adsorption, IR, DR-UV-vis and DRIFT spectroscopic techniques, were used for characterization of these materials.

Catalyst design principles are summarized and discussed to illustrate the effective development of catalysts that would meet the requirements of the catalytic application (Table 1).

Iron-containing materials have been tested as catalysts for wet phenol oxidation with H_2O_2 at pH = 6.2. The following parameters influencing catalytic properties of these materials and stability to leaching of metal from the solid are considered: *a)* Fe and Al content in the samples; *b)* agglomeration and isolation of iron ions; *c)* pH of the synthesis mixture. It was shown that the increase in Al/Fe ratio, which depends on pH of the synthesis mixture, reduces to the decrease in the formation of oligomeric iron species and favours the increase in reaction rate. The catalytic activity of Fe,Al-containing samples is higher than that of Fe-containing samples. The increase in Al content favours the increase of the strength of basic sites of Fe-containing samples detected with $CDCl_3$ adsorption. The insertion of Al leads to the changes in type and content of OH-groups which facilitate the sorption-desorption processes of reagents. Activity of Fe,Al-MMM(4.4) is higher than that of Fe,Al-PILC(4.4) at 40-50°C due to the decrease of diffusion limitation.

Table 1: Phenol oxidation with H_2O_2 in the presence of Fe-containing samples

	S_{BET} $m^2 \cdot g^{-1}$	d_{001}	Fe/Al wt/wt	Time[A] h	Fe leaching wt %
Na-clay	113	15	0.8/5.6	30	-
Fe-PILC	136	16	1.1/5.6	2.0	5.4
Fe,Al-PILC(4.4)	215	18	1.5/9.8	1.5 0[B]	<0.1 -
Fe-MMM(2.4)	930	38	1.7/0	10.0[C]	0.2
Fe,Al-MMM(2.4)	1518	39	1.1/3.1	3.5[C]	6.7
Fe,Al-MMM(4.4)	1315	38	1.1/6.4	1.0 2.5[B]	<0.1 <0.1

The reaction condition: PhOH 1 mM, H_2O_2 14 mM, Fe,Al-PILC 1 $g \cdot L^{-1}$, pH 6.2, 60°C; [A] Time of 100% conversion of PhOH; [B] 40°C; [C] 60°C (pH of the synthesis mixture is shown in parentheses)

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Technological characterization of peloids maturated with montmorillonite and sepiolite

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Dermatological semisolid preparations such as thermal muds (peloids) require a suitable rheological profile in view of their manipulation and therapeutic efficacy. Indeed, the rheological properties of such preparations affect the entire life of the formulation, since the mixing, filling and packaging until use and "in vivo" behaviour [1]. From a broad point of view, these formulations must be consistent at rest and easily to pour and spread when applied. However, the rheological behaviour of a clay/water system may change over time, leading to unstable and inadequate formulations [2]. These semisolid systems must therefore be considered as complex materials whose stability must be evaluated on the basis of rheological analysis as complete as possible. With these premises, aim of this work was to study the rheological behaviour of thermal muds matured under different conditions as part of a wider research whose focus is on standardizing the development of therapeutic muds.

Peloids of montmorillonite or sepiolite in mineral water from Graena Spa (25 % w/w) were prepared by using a mechanical shaker (Ultraturrax T25, Janke and Kunkel GMBH & Co., G) at 10,000 rpm for 5 minutes. Peloids were maturated in static conditions (without agitation) and with manual agitation every seven days, for a maximum period of three months. At specific times (time zero, one, two and three months), complete rheological analysis of aliquots of the peloids were taken by means of a rotational rheometer (Bohlin ® CS, Bohlin Instrument Division, Metrics Group Ltd., UK). The analysis was conducted using a cone/plate (CP 4 / 20) measurement system at 25°C, applying increasing and decreasing shear rate in the range 70 - 800 s^{-1}.

Flow curves of standardized systems prepared with montmorillonite or sepiolite showed typical profiles of viscoplastic fluids, with yield values depending on the type of clay mineral and conditions of maturation. The samples also showed rheological time-dependent properties, with hysteresis areas. In particular, montmorillonite samples showed thixotropic behaviours, whereas sepiolite systems were anti-thixotropic when prepared, changing to thixotropic as a result of dynamic maturation. It can be concluded that dynamic maturation is preferable to static conditions, in view of the rheological behaviour (thixotropy) of peloids formulated with laminar and fibrous clays.

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Removal of Cu^{2+} from aqueous solutions by using bentonites as adsorbents

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Adsorption of heavy metal cations on clays is of great scientific interest due to their toxicity and harmfulness. Numerous papers on the use of bentonites as adsorbents have been published, e.g. [1]. This work is focused on various effects on the sorption of Cu^{2+} on two commercial bentonite products prepared from two Slovak bentonites Lieskovec (S011) and Jelšový potok (S110).

They were characterized by powder X-ray diffraction (XRD) and infrared spectroscopy (FTIR). XRD analysis revealed smectite to be the major component present in both samples, while the accessory minerals were quartz, mica and feldspar in both samples and kaolinite in S011. FTIR spectra helped to identify montmorillonite compositions (Fig. 1).

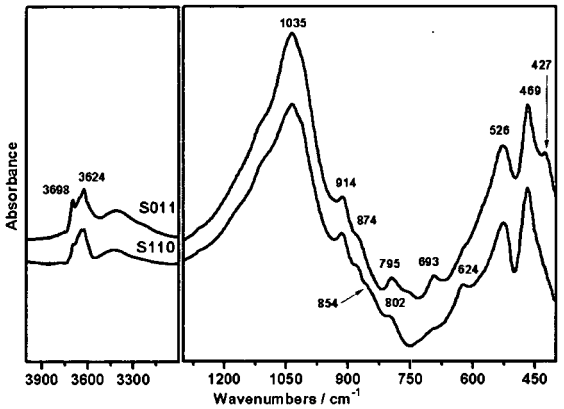

Fig. 1: The IR spectra of S011 and S110.

AlAlOH bending vibrations at 915 cm^{-1} show montmorillonite and the band at 854cm^{-1} (AlMgOH) confirm higher Mg for Al substitution in S110 while the AlFeOH component at 874 cm^{-1} and the absence of an AlMgOH band reflect higher Fe and lower Mg contents in S011, thus causing the lower cation exchange capacity (CEC) of S011. CEC as determined by the Cu-triethylenetetraamine method was 40 mmol/100 g for S011 and 79 mmol/100 g for S110. Specific surface area determined by EGME (Ethylene Glycol Monoethyl Ether) adsorption was 386 m^2/g for S011 and 459 m^2/g for S110.

The adsorption experiments were carried out using the batch technique. The effects of pH, contact time and initial Cu^{2+} concentration were tested. The adsorption was strongly dependent on pH of the medium; the uptake of Cu^{2+} was increasing from pH 2.0 to 7.0. At higher pH values, formation of copper hydroxyl compounds affected the sorption results. The uptake of Cu^{2+} was rapid and it increased with increasing metal concentrations. The sorption percentage decreased with increasing concentration of Cu^{2+}. Langmuir adsorption isotherms were found to fit best the obtained experimental data for both bentonites.

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X-ray diffraction and desorption study of the phases formed upon calcinations synthetic layered double hydroxides

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The thermal and kinetic parameters of heating processing of LDHs, providing a complete lack of transfer of sorbed substances into the liquid phase due to the formation spinel structures were determined.

Traditional sorbents can undergo the reverse process of desorption and ion exchange, resulting in a possible penetration of pollutants into the environment. Prevention of this process can be achieved by turning hydroxide sorbent in spinel. The purpose of this work is to define the area of formation spinels, ensuring the absence of pollutants desorption:

$$Mg_xAl_yCr_z(OH)_m \rightarrow xMgO \cdot y/2Al_2O_3 \cdot 2/zCr_2O_3$$

The thermogravimetric analysis allows to trace the processes occurring during heating of hydroxide materials. These experimental curves show the temperature of the beginning of thermal decomposition of the original samples and a deep restructuring of compounds. Thermogravimetric curves represent the mass loss of the sample during heating. These results allow to characterize the thermal stability of the hydroxide ion - exchangers. LDHs were saturated by solution containing of chromate ions. Then LDHs were dried. Samples of the sorbent with adsorbed chromate ions were selected and placed in a muffle at regular intervals, at certain temperatures.

The temperatures above 500°C the irreversible dehydration with the formation of spinel structure take place. This feature of LDHs, are essential for their use as adsorbents of toxic anions. Heat treatment can bond the layers to form insoluble compounds and burying without fear of the reverse process of desorption under the influence of external conditions. That may take place traditional for adsorbents such as activated, but not heat treatment LDHs take place. There is a formation of new oxides phases at the heat treatment.

Table 1: The concentration of chromate ions after desorption

τ\t	150°C	250°C	400°C	600°C	800°C	1000°C
5	$1{,}51\cdot10^{-5}$	$0{,}88\cdot10^{-5}$	$0{,}51\cdot10^{-5}$	$0{,}25\cdot10^{-5}$	$0{,}19\cdot10^{-5}$	**0**
15	$1{,}28\cdot10^{-5}$	$0{,}86\cdot10^{-5}$	$0{,}49\cdot10^{-5}$	$0{,}25\cdot10^{-5}$	$0{,}18\cdot10^{-5}$	**0**
30	$1{,}09\cdot10^{-5}$	$0{,}81\cdot10^{-5}$	$0{,}42\cdot10^{-5}$	$0{,}24\cdot10^{-5}$	$0{,}18\cdot10^{-5}$	**0**
60	$1{,}05\cdot10^{-5}$	$0{,}76\cdot10^{-5}$	$0{,}39\cdot10^{-5}$	$0{,}23\cdot10^{-5}$	**0**	**0**

In the table are shown the area of spinels formation. Analyzing the obtained data, we may say that with increasing of temperature and time of heat treatment the process of desorption is minimized. After 800°C the spinel structures formed and the process of desorption becomes impossible. We may assume that the used anionic sorbent can be subjected to heat treatment at 800°C, and after that the processes of burial of the sorbent is not risky. It was shown that at temperatures above 1000°C and the residence time more than 2 hours the shpinel structures will be disintegrate. The thermal and kinetic parameters of heating processing of LDHs, providing a complete lack of transfer of sorbed substances into the liquid phase due to the formation spinel structures were determined.

New insights on the humic acid uptake by homoionized montmorillonite and CTMA-montmorillonite

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Contaminated water is one of the biggest problems in the world, not just the low percentage (2.5%) of fresh water available, but also the unequal distribution in the world is still worrying. To improve the drinking water quality various procedures can be applied according to the characteristics of water contamination.

Particularly, the organic matter (OM) in water is responsible, among others, of the water turbidity and enables to the formation of stable aggregates with metals, commonly associated with high levels of microorganisms. The OM consists mainly of humic and fulvic acids, difficult to remove with conventional techniques used in flocculation water treatment processes. As an alternative to conventional drinking water treatment and to reduce the humic acid content, this paper presents the use of homoionic montmorillonites and a cetyl trimethyl ammoniun-montmorillonite (CTMA-MMT) to uptake humic acid of water.

The raw montmorillonite used (Rio Negro Province, denoted MMT), contains 84% montmorillonite and 4% quartz and 12% feldspar as impurities. Fractions of MMT sample were homoionized with Na, Ca, K and exchanged with CTMA (1 CEC). Zeta potential determinations of MMT, HA, CTMA-MMT and CTMA-MMT+HA were realized, to identifie their surface charge. The HA adsorption isotherms were determined on all samples in absence and presence of ionic strength (10^{-2}M of the respective chloride cation solutions). The samples without and with HA were characterized by XRD, specific surface determined by water and N_2 adsorption and apparent diameter (Dapp).

The Sw values showed an increase order related to the cations exchanged: CTMA-MMT <K-MMT <MMT <Na-MMT <Ca-MMT. The presence of HA causes a decrease in these values showing the hydrophobic character of the new surface with the HA complex. While the SN_2 values showed almost inverse correlation, confirming the non-polar status of N_2 and its difficulty to enter in the montmorillonite interlayer. The Dapp values follow inverse correlation to that found for Sw on all samples.

Negatives surface charge values were found for both HA and MMT in all pH range studied (from pH 3 to 10). The CTMA exchange originated in the CTMA-MMT sample shifted the surface charge to positive values and the HA adsorption decreases the positive surface charge values found in CTMA-MMT sample.

The XRD spectra showed a shift of the reflection peak d (001) respect to the MMT dependent of the water layer related to the interlayer cation in the following order: Na-MMT < K-MMT< MMT< Ca-MMT< CTMA-MMT. The presence of HA, in all samples causes a slight decrease in the interlayer spacing, possibly originated by the complex formed between the AH with the interlayer cation.

The HA adsorption, in the absence of ionic strength, for all homoionized samples showed a Langmuir type behavior, while the HA adsorption on CTMA-MMT showed a high adsorption at low HA concentrations and max adsorption kept constant with HA concentration increase.

In ionic strength presence (10^{-2} M) only the Ca-MMT sample showed a different behavior than that of Langmuir adsorption.

Formation of brom-pyromorphite as the effect of lead and phosphates sorption on surfactant-modified smectite

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Sorption on organo-modified clays (e.g. smectites) is one of the methods used for the removal of toxic compounds (inorganic anions and cations, neutral organics) from solutions [1]. The objective of this study was to evaluate potential application of surfactant-modified smectite for sorption of PO_4^{3-} and Pb^{2+}. Precipitation of brom-pyromorphite $Pb_5(PO_4)_3Br$ is observed when Br-surfactant is used for modification.

Sample of smectite was modified with the use of amine hexadecyltrimethylammonium bromide (HDTMA-Br) in the amounts of 2.0 Cation Exchange Capacity (CEC) of the clay. HDTMA is a large organic cation, that in this experiment was used in bilayers form (surfactant concentration was higher than a critical micelle concentration). It changes the charge on natural smectite from negative to positive, but it does not use up all negative sites. Therefore, it is possible to use surfactant-modified smectite as a sorbent for various classes of aqueous solutes.

Modified smectite was reacted with solutions containing 5 to 20 mM/L of Pb or PO_4 ions at initial pH from 2 to 5. In the first step, surfactant-modified smectite was reacted with PO_4 or Pb ions. In the second step, Pb-sorbed samples from the first step were reacted with solution containing PO_4 while PO_4-sorbed samples from the first step were reacted with Pb ions.

Sorption of PO_4 was highest on Pb–surfactant-modified smectite, while sorption of Pb was highest on surfactant-modified smectite with no PO_4 pretreatment. In both cases sorption was highest at pH = 5. Also, formation of brom-pyromorphite $Pb_5(PO_4)_3Br$ was noted in the reaction products, which was identified with the use of X-ray diffraction and SEM. Pyromorphite forms crystals either in the volume of solution (homogeneous crystallization: reaction of aqueous PO_4 with Pb desorbed from ion-exchange positions) or on the surface of a surfactant-modified smectite (heterogeneous crystallization: Pb ions from solution react with PO_4 absorbed and still present on the organic HDTMA bilayers) (Fig. 1).

Fig. 1: SEM microphotographs of brom-pyromorphite formed in the reaction of aqueous Pb^{2+} and PO_4–surfactant-modified smectite (heterogeneous crystallization).

Acknowledgements: We gratefully acknowledge support of the MNiSW through grant N N525 461236.

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Clay characterization in sediment cores from Novigrad sea area, Croatia

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The Novigrad sea is a small, semi-closed bay located in the central part of the eastern Adriatic coast, about 20 km north of Zadar (Fig. 1). It is connected to the Adriatic sea in the northwest by Velebit channel and the Karin sea in the southeast. In the surrounding area several bauxite deposits have been exploited for many years with the transshipment port situated in the Novigrad sea. Assessment of the influence of dispersion of bauxite dust by wind and water from dozens of open bauxite pits and waste disposal site of an abandoned alumina plant in the vicinity of the Novigrad sea on the environment is necessary.

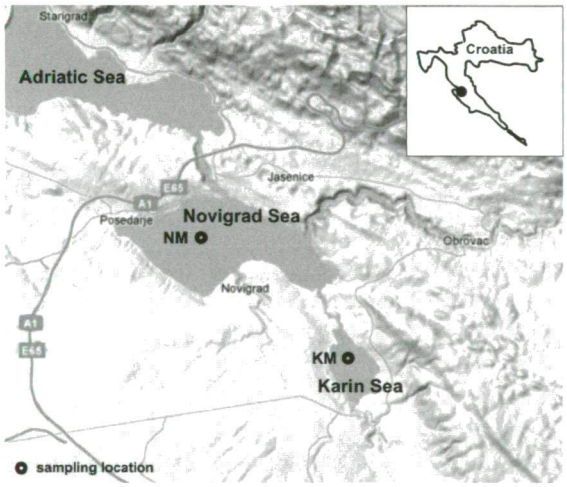

Fig 1: Map of the Novigrad sea area.

Clay minerals have an important role in aquatic systems, as both a carrier and source of pollutants. Therefore, detailed characterization of clay content in recent marine sediments is a prerequisite for an assessment of source and distribution pathways of contaminants. In case of high carbonate content of studied sediments, removal of carbonate phases prior to detailed clay analysis is necessary.

Removal of carbonate minerals from sediments at room temperature was investigated by three different acids, hydrochloric acid (0.5M HCl), acetic acid (4M CH_3COOH) and formic acid (4M HCOOH). Our aim was to evaluate the effects of different chemicals on the properties and structures of present clay minerals in order to develop the optimal procedure for further detailed characterization of clay minerals in marine sediments of the Novigrad sea area.

The analysis was performed on two sediment cores of different carbonate content, one from Novigrad sea **NM** (~19% $CaCO_3$) and one from Karin sea **KM** (~31% $CaCO_3$) (see Figure 1). X-ray diffraction was used to obtain mineralogical composition of the bulk, carbonate free, as well as glycolated and heat-treated (at 450°C and 550°C) samples.

Results indicate that the bulk samples are dominantly made up of carbonates (calcite – Ca and dolomite – D), quartz (Q) and halite (H), while clay minerals (chlorite – Cl, illite/mica – I/M) occur as minor phases. Detailed characterization of clay content of samples after the carbonate removal by different acids will be discussed.

The surface modification of clays for removal of toxic Se-oxyanions

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Selenium compounds represent serious threat for environment and human health. They arise mostly anthropogenically and occur in organic or inorganic forms (predominantly as SeO_3^{2-}, SeO_4^{2-}) in natural systems [1]. The adsorption is one of the applicable methods of these toxic substances removal. Clays (kaolines, bentonites) can be classed as technologically important adsorbents. They are characterized by the low value of pH_{ZPC} (zero point of charge) and attract mostly cations. It is possible to increase their anionic affinity for obtaining the efficient and inexpensive adsorbents by a simple chemical Fe, Al, Mn-modification [2-4]. The aims of this work is the preparation of new low-cost adsorbents, their qualitative and quantitative description, the adsorption of toxic SeO_3^{2-}, SeO_4^{2-} oxyanions and the verification of their stability on prepared adsorbents.

Mineralogically pure clays were used for surface changes study – two kaolines from West Bohemia with higher content of kaolinite (> 60 %), bentonite (Riedel de Haën, Germany) containing mostly montmorillonite and standard Ca-rich montmorillonite SAz-2 (Arizona, USA).

The initial concentration of Se in model aqueous solutions was 10 - 40 mg/L and the amount of solid samples ranged from 1 - 10 g/L. Sorption processes ran 72 h. Kinetic experiments were carried out as well.

The sorption capacities of clays increased markedly after the modification (from 0 to 20 mg/g). The kinetic study revealed that 8 h was needed for Se removal. The stability of Se on the solid surface was checked by leaching tests which confirmed the release of it in the range of 0.1 – 2 %.

XRD, XRF, S_{BET}, IR and pH_{ZPC} measurements were used for the characterization of the surface changes during the treatment and next adsorption. The surface of newly prepared adsorbents was amorphous and porous. Specific surfaces (BET) did not change notably after the treatment. The pH_{ZPC} of treated clays moved from 6 to 10.

Acknowledgements: This work was supported by research program MŠMT č. 21/2010 (ČR).

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Bioleaching effects and binding of Zn on clay, iron and manganese minerals

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Water reservoir Ruzin I in the region of Eastern Slovakia is a long – therm problem of sediments contaminated with heavy metals (Zn, Cd, Ni, Cu, Hg, As) as a result of mining and metallurgical activities in the basin. The focus of this work is to assess the mobility of Zn in sediment samples in the presence of clay minerals and iron oxides. X-ray diffraction analysis of sediment confirmed presence of quartz, illite, kaolinite and montmorillonite (Philips XPERT, Germany).

Table 1: The amount of Zn, Fe and Mn in the sediment (AAS, Varian AA-30, Australia), BL –bioleaching with Bacillus megaterium

Elements	Before BL (mg/kg)	After BL (mg/kg)	TV (mg/kg)
Zn	427	192	140
Fe	44 600	24 500	-
Mn	1315	1210	-

TV – Target value by MP MŽP SR No. 549/98-2

Sequential extraction method by Tessier was applied to obtain information about chemical binding Zn in the sediment matrix. Adsorption of Zn on Fe and Mn oxides was confirmed in 55% (wt) and in the structure of clay minerals of the so-called residual fraction of Zn was found in 28 % (wt). Heterotrophic bacterial species *Bacillus cereus* and *Bacillus megaterium* presented in the sediments were identified by biochemical BBL identification system. They control mobility of Zn in Fe – Mn oxides and clay minerals. Figure 1 presents kinetics of Zn dissolution in bioleaching medium (containing glucose as carbon source for active heterotrophic bacterial species) and comparing the effect of inoculation of *Bacillus megaterium* and *Bacillus cereus.*

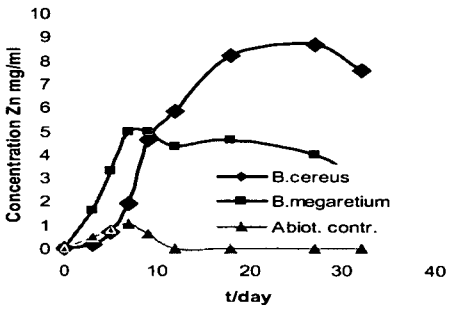

Fig. 1: Kinetics of bioleaching Zn from sediment inoculated with Bacillus cereus and Bacillus megaterium bacterial strains.

Efficiency of discontinous bioleaching Zn from contaminated sediments lasting 6 months with use selected bacterial species were as follows: *Bacillus cereus* 71 % > *Bacillus megaterium* 64 %. These bacterial strains use for their metabolism Fe/Mn oxides and clay minerals therefore they increase the mobility of Zn in aquatic sediments. This principle is usable in prospective *in-situ* remediation of contaminated bottom sediments.

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Decontamination processes for removal of some pharmaceuticals from aqueous systems

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Pharmaceuticals have become the inherent part of current modern society. Several pharmaceutical substances have been annually used in amounts up to hundreds of tons in some countries [1]. Therefore the big attention has been paid to the influence of these compounds on the environment. After their application, pharmaceutical substances are excreted in an unchanged form or eventually in the form of water-soluble metabolites [2].

The pharmaceutical industry, hospital facilities, private households and landfills are the next inconsiderable sources of these contaminants [3]. That's how the pharmaceutical substances reaches the sewage water and regarding they are not completely eliminated in sewage treatment plant [4]. Therefore, they infiltrate into the ground water, surface water and drinking water. They also settle in river sediments and water reservoir sediments.

The aim of this work is to find suitable decontamination processes for the removal of mass-used pharmaceutical substances from aqueous systems. For this purpose, the sorption properties of natural inorganic materials (especially clay minerals) have been used. Sorptions have been carried out from the model solutions of analgetics representatives (e.g. paracetamol, salicylic acid). The sorption capacities of clay minerals have been determined. In the next part of this work, the influence of reaction conditions on the sorption process has been studied.

Acknowledgements: This work was the part of the project P210/10/0938 (Grant Agency of Czech Republic).

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Modification of the montmorillonite with the cationic and non-ionic surfactants

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Many industries give rise to dye-bearing effluents in their production processes. Textile industries, particularly, are major consumers of water and release a fair amount of color in their effluents. It follows that dyes need to be removed before the effluents are discharged into rivers. However, this has always been a major problem because of the difficulty of treating such wastewaters by conventional methods. Biological procedures, although widely utilized in the removal of color, are very inefficient because of the low biodegradability of dyes. A variety of other methods, including coagulation, chemical oxidation, photocatalysis, and electrochemical and adsorption techniques [1], has been examined.

Adsorption techniques have been widely applied to the treatment of industrial wastewater containing dyes, heavy metals, and other inorganic and organic impurities. In some cases, it is possible to recover the adsorbed dye through desorption and to reuse the large amounts of water employed by textile industries. The adsorption phenomenon has been known since the 17th century when it was discovered that porous materials have the property of adsorbing gases and, subsequently, the same phenomenon was observed for solutions. Adsorption has been found to be one of the most efficient physicochemical processes, superior to many other techniques for water reuse in terms of the simplicity of operation. If the adsorption system is designed correctly, it will produce a treated effluent of high quality. Activated carbon has been widely used for this purpose because of its high adsorption capacity. However, its high cost sometimes tends to limit its use. Several nonconventional, low-cost adsorbents have also been tried for dye removal.

The present work is aimed to study the adsorption capacity and mechanism of removal of industrial anionic textile dye Acid Red 88 by organobentonite. The organoclay adsorbent used was prepared by modification of commercial Nanocore montmorillonite with octadecyl ammonium bromide (ODTMA) and compared with materials prepared with the non-ionic surfactants [2] containing the same hydrophobic C_{18}- end-chain and various repetitive units of hydrophilic poly(ethylene oxide) (PEO) segments.

The layer spacing of the ODTMA- and $C_{18}PEO_n$ - smectite composite was well preserved during water washings, indicating stability of cationic organoclay and higher molecular weight non-ionic surfactant molecules in the interlayer galleries. The non-ionic surfactant treatment preserved >90% of the CEC of the smectite while ODTMA-clay lost almost all cation exchange capacity. The surfactant-montmorillonite composites effectively removed aromatic textile azo dye from water solution while untreated smectite did not adsorb these molecules. The enhanced adsorption of the aromatic compounds is attributed to the aliphatic segments (C_{18}) of the five surfactants, however ODTMA-montmorillonite showed highest sorption capacity for naphthalene based textile dye AR88.

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Geopolymers: new products for sustainability of the environment

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Geopolymerization is the process of polymerizing minerals with high silica and alumina at low temperature by the use of alkali solutions. Geopolymers could be a substitute for Portland cement and for advanced composite and ceramic applications. The geopolymer technology would eliminate the need for energy requirement as they may be cured at ambient temperature.

Current research at the University of Jordan concentrates on developing building products (geopolymers) through geopolymerization. The goal is to produce low cost construction materials for green housing. The produced construction materials are characterized by high strength, high heat resistance, low production cost, low energy consumption, and low CO_2 emissions.

The results have confirmed that natural kaolinite satisfy the criteria to be used as a precursor for the production of high quality inexpensive, stable materials. Geopolymeric products gave a high unconfined compressive strength values up to 52 N/ mm^2 for dry test. This value has been increased to 57 N/ mm^2 by the immersion of the geopolymerzed products in 10% solution of triethylene glycol.

The addition of rock wool gave the maximum unconfined compressive strength up to 90 N/ mm^2 after heating to 500°C for one day. The addition of zeolitic tuff as a filler has increased the adsorption capacity of the polymerized products towards heavy metals. This result enables the use of geopolymers in waste water treatment plants.

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Environmental impacts associated with a landfill in the municipality of Zakynthos, Greece

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Landfills are widely used as a disposal method for municipal solid waste in most European countries. However, landfills if not properly managed, may pose a serious threat to the environment due to leachate run-off and contaminant transport in the surrounding environment. Landfill leachates can contaminate groundwater and surface water [1]. The mineralogy of the clay material used in the landfill liners controls the mobility of contaminants therefore, clay mineralogy is important in order to minimize migration of pollutants in the environment.

To evaluate the environmental risks associated with a landfill in the municipality of Zakynthos, Western Greece, samples were collected from the material used in the landfill and from sediments from a stream system, in the vicinity of the waste disposal site. Surface and groundwater samples were collected and analysed to determine some geochemical parameters usually considered to be indicators of pollution from solid waste disposal. The mineralogical composition of all samples was determined by XRD and revealed the presence of calcite, quartz, albite, smectite, chlorite, illite and mixed-layer chlorite-smectite. Trace element analyses showed that the abundance in Cu and Zn is higher in the stream sediments compared to the uncontaminated samples and since stream sediments are in contact with run-off waters from the landfill this could be an indication of contamination from the landfill. According to drinking water standards, the concentrations of all trace elements in the studied waters were below the maximum contaminant level values given by European Council Directive [2] and WHO [3]. Finally, the concentrations of Cl^-, SO_4^{2-}, NO_3^- and NO_2^- in the water samples exceeded the average permissible concentrations and are considered as human induced contamination from the landfill.

Acknowledgements: This research was funded by the University of Patras through the K. Karatheodoris basic research funding scheme.

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ZnS particles deposited on montmorillonite and their photocatalytic efficiency for CO_2 reduction

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Semiconductors such as metal sulphides and metal oxides appear to be very promising materials for photocatalysis due to rapid generation of electron–hole pairs by photoexcitation and highly negative reduction potentials of the excited electrons. CO_2 is a well know greenhouse gas. To convert it by force, a severe condition of high pressure and high temperature is required. The reduction of CO_2 using photocatalysts is one of the most promising methods because CO_2 can be reduced to utilizable compounds (e.g., methanol, ethanol, methane, hydrogen) by irradiating with UV light at room temperatures and low pressure [1,2].

The ZnS nanoparticles were deposited on montmorillonite (MMT) in the presence of cetyltrimethylammonium (CTA). UV spectrometry and transmission electron microscopy proved the formation of nanoparticles with the diameter ranging from 3 nm to 5 nm. Selected area electron diffraction confirmed the existence of romboedric ZnS. Photoluminiscence spectra exhibited a strong emission band between 300 nm and 600 nm, which was assigned to transitions due to sulphur vacancies in ZnS. The prepared ZnS-montmorillonite (ZnS-MMT) nanocomposite was used for the photocatalytic reduction of CO_2 providing considerably high efficiency which exceeded the results of commercial TiO_2 Degussa P25 5-6 times. Methane, methanol, carbon monoxide and hydrogen were the main reduction products of the reduction. The stability of ZnS against oxidation was proved by the determination of sulphate by capillary isotachophoresis.

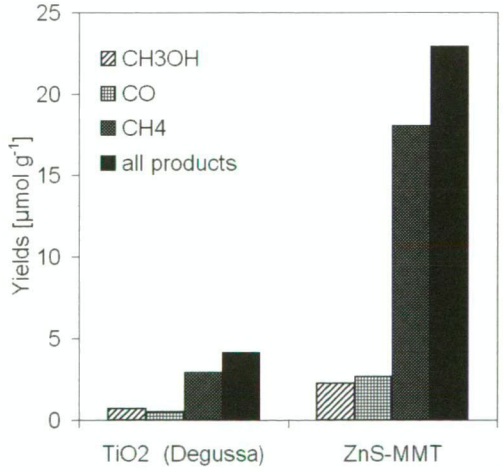

Fig. 1: The comparison of product yields per gram of the photocatalyst.

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Effect of clay content on As, Se-adsorption in soils

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The aim of this work is the study of soil adsorption properties depending on the portion and characteristics of clay fraction. Soil samples from protected area Cesky Kras and Labe river basin (Middle Bohemia, Czech Republic) used in this research, where the elevated concentration of As and Se have been observed. The samples were dried at laboratory temperature, grinded, fractioned and digested in the microwave mineralization device MWS-2 Berghoff. The amount of As and Se in mineralised samples was assessed by HG AAS. The content and type of clay mineral presented in the soil samples were determined by X-ray diffraction and subsequently, the sorption capacity of soils and the stability of adsorbed As and Se under different conditions (pH, Eh) were investigated [1]. pH_{H2O}, pH_{KCl} [2] and pH_{ZPC} [3] were also measured.

Table 1: Concentration of arsenic and selenium in investigated soil samples; A1-A3 – Cesky Kras protected area, B1-B3 – Labe river basin

	c [mg/kg]		pH	
	As	Se	pH(H_2O)	pH(KCl)
A1		2.7	6.5	6.7
A2		2.1	7.2	6.9
A3		14.4	7.0	6.7
B1	25.1		7.5	7.1
B2	35.3		7.5	7.4
B3	26.5		7.2	7.1

The results in Table 1 show elevated As/Se concentration in all investigated samples. The presence of clay and hydrated oxides and/or Fe-oxyhydroxides influenced sorption properties of soils.

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Clay minerals and landslides on the slopes of Medvednica Mt. in Zagreb city area (Croatia)

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The landslides problem is pronounced on the slopes of Medvednica Mt. in Zagreb city area. Therefore, in 2005-2007, Zagreb city government engaged Croatian Geological Survey to make detailed engineering geological map M 1:5.000 of this area.

The landslides problem occurrs in the Miocene and the Pleistocene deposits, so those sediments were the main object of investigation. Litological composition of the Miocene deposits varies from marls, limestones, silts, sands and sandstone to rarely represented coarser-grained sediments such as conglomerates and breccias. The Pleistocene sediments which discontinuously cover the older deposits consist of poorly sorted clays, silts, sands and gravels.

The aim of this study was to determine relationship between clay mineralogy and occurence of landslides. Apart from standard engineering-geological investigations (SPP tests, pocket penetrometar, wane shire tests, liquid limit and shrinkage limit, grain size distribution, uniaxial compressive strength test), mineralogical investigations of sediments (XRD, DTA, SEM and chemical analysis) were included.

It was found that the largest number of landslides is related with Pontian silty-marl deposits (7.1-5.6 Ma) and Pleistocene silty-clay deposits (1.8 Ma – 10.000 years). These deposits contain continuous layers with clay minerals having high to very high and extremely high plasticity. In the Pontian sediments the most common clay minerals are smectite and illite / muscovite, and in some samples small quantities kaolinite and chlorite appear [1] [2]. Vermiculite and illite / muscovite are the most common clay minerals in the Pleistocene deposits. Kaolinite is present in almost all Pleistocene samples [1]. Smectite occurs in very small quantities only in certain samples, while chlorite is present mainly in the sandy and the silty fraction of these deposits.

In the wider Zagreb city area landslides are activated mainly during the first spring months, which is associated with content of water in soil, high groundwater levels and increased yield sources. It is known that increasing the amount of water in soil leads to swelling of clay minerals such as vermiculite and smectite. The presence of swelling clay minerals in the Pontian and the Pleistocene depositescausee cause the instability of slopes in the wider Zagreb city area. Differences in levels of slope instability are related to the different amount of expandable clay minerals in sediments and differences in water content in soil that directly influence the behavior of expandable clay minerals. Other factors which have important influence on instability of slopes are tectonics, shear strength, increase of the incline slope and antropogenic influence.

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Sorption of cadmium (II) by the natural bentonite and magnetic clay composite

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The objective of this work is to compare the removal of cadmium (II) by the natural bentonite and composite, prepared by magnetic modification of the clay. The composite material was prepared by the method of precipitation from the solution of ferrous and ferric salts (Fe^{2+}/Fe^{3+} = 0.5), where the bentonite was added prior to the reaction. The weight ratio of bentonite to iron oxides was 5 to 1. The structural and surface study realized by XRD method, FE-TEM and low nitrogen adsorption method showed that the surface properties of the composite (Table 1) were affected by the precipitation of maghemite and goethite in agglomerated form.

Table 1: Surface parameters of the investigated samples obtained from the low temperature nitrogen adsorption method (S_{BET} – specific surface area, V_a – total pore volume, V_{micro} – volume of micropores, S_t – external surface area)

Sample	S_{BET} [$m^2 g^{-1}$]	V_a [$cm^3 g^{-1}$] STP	V_{micro} [$cm^3 g^{-1}$] STP	S_t [$m^2 g^{-1}$]
bentonite	39.44	0.096	0.006	25.43
composite	90.68	0.187	0.002	84.23

The sorption properties were examined under different conditions such as pH of the model solutions, contact time and initial metal ion concentration. The adsorption of cadmium (II) was dependent on the pH of the solution as well as the concentration of ions. The optimal pH for removal of cadmium (II) was found equal 5. The batch type experiments with the natural bentonite and composite material were first conducting using metal ion solutions ranging from 10 to 700 mg L^{-1}. Maximum adsorption capacities (61.35 and 63.29 mg g^{-1} for the bentonite and composite, respectively) were calculated using linearized Langmuir isotherm. Different adsorption rates observed in the low initial metal ion concentrations indicated the further study of adsorption at lower ranges. The highest efficiency of the composite material (more than 98 %) was observed in the range from 1 to 10 mg L^{-1}, Fig. 1.

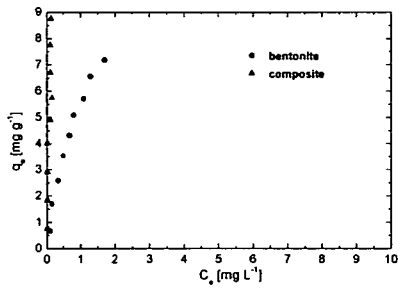

Fig. 1: Sorption of Cd(II) ions on the natural bentonite and composite material in the low initial metal ion concentration range 1 – 10 mg L^{-1}, sorbents dose 1 g L^{-1}, initial pH 5, contact time 24 hours.

Removal of heavy metals at low concentrations from aqueous environment is generally difficult, but the studied composite material showed very good sorption ability especially in these conditions. Therefore it seems to be convenient to use it in desposal of metals from aqueous solution, where their concentration is very low, but still harmful, as well as for the final purification of pre-treated waste waters.

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Aquocomplex structure in the interlayer space of swelling high-charged micas

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The structure of the interlayer region of swelling high-charged micas is one of the fundamental problems of clay science. The mobility of the cations is important for describing chemical reactions in the environment as well as for estimating the environmental behaviour of metal ions. However, the chemical species of metal cations at solid-water interface in the interlayer space of swelling high-charged micas is still not clearly understood.

It is known that cation sorption is governed by cation size and charge, but the location of structural charge within a clay layer and the existence of hydrophobic patches on its surface provide important modulations. On one hand, larger the interlayer cation, greater the influence of clay mineral structure and hydrophobicity on the configurations of adsorbed water molecules. On the other hand, larger hydrated radius means that the cationic center of charge is farther from the clay surface so the clay-cation electrostatic interaction is weaker.

The aim of this research was the systematic study of hydrated swelling high-charged M-Mica-n,-where n represents the layer charge equal to n=2, 3, 4 and M is the interlayer cation, ($M=Na^+$, Li^+, Mg^{+2}, Al^{+3})- using Thermal Analysis (ATD/TG), X-ray Diffraction and Solid State NMR.

Na-Micas-n (n=2,3,4) prepared as reported by our research group were used as starting materials.[1] M-Micas-n were prepared by cation-exchange reaction, in accordance with the method described by Powell et al. [2]

The results obtained with TG measurements revealed that the cation hydration state did not only depend on the cation nature, as expected in solutions, but did on the Mica layer charge. Hence, an interaction between interlayer cation and the basal plane of the tetrahedral sheet of Mica could be infered. It was confirmed by ^{29}Si MAS NMR and the variation of the 060 reflection. Therefore, it can be concluded that the nature of the cations and Mica determine the equilibrium between inner-sphere and outer-sphere complex formation.

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Vertical and horizontal distribution of ^{137}Cs in Pest County, Hungary

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This paper presents the results of measurements of ^{137}Cs in soils which were sampled in Pest County, Hungary. The studied soil samples of 45 soil monoliths from TIM (Soil Information and Monitoring System) were collected in 1992. The ^{137}Cs content has been determined for all locations by gamma spectroscopy and found that only the upper layer of soil (0-30 cm) contains ^{137}Cs from the all layers (0-30, 30-60, 60-90, 90-120, 120-150 cm). Cesium-137 concentration in these layers ranged 0.7 ± 0.5 Bq/kg to 41.3 ±1.5 Bq/kg. These activity values were illustrated on a map that can be consider as the first detailed cesium map in Hungary. We found salient value (31.7 Bq/kg and 41.3 Bq/kg) compared to the average activity (5.8 Bq/kg) at two points of the sampling sites. One of them is at Gödöllő Hills and the other is at the western foot of Buda Mountain. It is known that there is a strong relationship between ^{137}Cs concentration and clay, as well as organic matter content of the soils [1,2]. This relationship was studied in details in soil samples from drilling in brown forest soil from the same location as the highest activity concentration (41 Bq/kg) occurred. Aggregate size fractions were separated using dry sieving technique and their clay mineral contents were determined by differential thermal analysis and XRD techniques. According to the results of these analyses, an amount of organic matter less than 40% and prevailing illite and kaolinite were determined in the sample. The amount of clay minerals was found closely proportional to cesium-137 activity in the aggregate fractions, which indicates the cesium fixation to these clay minerals. For analyzing the vertical distribution and migration of cesium, a soil profile at the same locality was studied. It was found that it is present in the upper 20 cm of the soil, indicating that penetration of cesium into the soil is very slow process here. 23 years after the Chernobyl accident most of the cesium activity is still in the top 16 cm, and the 78% is located in the top 3 cm. This corresponds to results of other studies [3,4] and suggests slower cesium migration than predicted earlier [5]. This prediction was applied in the framework of convective-diffusional model using time independent diffusion coefficient and convection velocity. Our results demonstrated for this site that either the migration speed is very low, or it is time dependent and slowed down during the last 10 years.

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Hungarian adobe as source of thoron

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Thorium (^{232}Th) is a naturally occurring radioactive element and thoron (^{220}Rn) isotope is the only one gaseous daughter of its decay chain. Thorium is estimated to be about three times higher abundance than uranium (^{235}U, ^{238}U) in natural environment including soils [1]. Thorium can also be quantifiable trace element like thoron source in clayey soils, which are the major raw materials of adobe houses beside straw.

Thoron, similar to radon (^{222}Rn) [2] in uranium (^{238}U) decay chain, has a high capability to enter the air of rooms from the walls of adobe houses, which makes possible to accumulate in indoor air, as well as its solid decay products as aerosols. Thoron has an effect in dose increasing which is underestimated in many cases. This is the reason why has not been done extended survey on it yet in Hungary.

The average of total annual effective dose from thoron is only 0.1 mSv [1], however, several studies [3-7] showed much higher values in dwellings made mostly by soil or soil bricks. Among these examples, annual effective dose goes up to about 5 mSv average [4]. It indicates that adobe houses in Hungary can be endangered by thoron more than other type of buildings, although they have several propitious features in many respects.

The main aim of this work is to obtain knowledge on possible risk from thoron and its source. Therefore, three distinct areas of Hungary have been selected to study. All of them have local soils suitable, experience and tradition for building adobe houses and a probability to be endangered by thoron. These areas are Sajó and Hernád Rivers' Valleys (NE-Hungary), where redeposited loess is typical, E-Mecsek Mts. (S-Hungary) and Békés County (SE-Hungary), where loess and alluvial sediments of Körös and Maros Rivers are prevailing, respectively [8].

Present work is focusing on Békés County where six settlements (Gyomaendrőd, Gyula, Kondoros, Sarkad, Újiráz, Vésztő) have been selected for detailed investigation based on geological and geographical differences and previous surveys, too. Experimental one-day indoor radon and thoron concentration measurement by RAD7 radon detector refers that fairly high thoron concentrations (even more than 400 Bq/m^3) can be detected in adobe houses of this area.

Soil samples of sought out adobe making places at selected six settlements have been collected, as well as abode samples at least from one dwelling of each sites. The origins of raw materials of adobe samples presumably are the mentioned adobe making places. Detailed study of the samples was done in laboratory, which refers that adobe can actually be a potential source of thoron.

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Reduced leaching of the herbicide metribuzin by using clay-gel-based formulations

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Herbicide mobility in soils has long been of concern for many reasons, including the following: (i) contamination of groundwater; (ii) reduction in efficacy due to herbicide leaching below the weed seed zone, which can reduce herbicidal activity and crop yield; and (iii) surface migration of the herbicide which harms neighboring crops.

To reduce herbicide leaching and increase weed control, new slow release formulations were developed by entrapping metribuzin within a sepiolite-gel-based matrix using two clay/herbicide proportions (0.5/0.2 and 1/0.2) (loaded at 28.6 and 16.7% active ingredient) as a gel (G28, G16) or as powder after freeze-drying (LF28, LF16).

A rheological characterization of the formulated products showed a viscoelastic behaviour as noted in the higher storage modulus G' than the loss modulus G'', within the experimental frequency range employed. A more detailed analysis of the rheological properties such as the apparent yield stress and plateau modulus indicated that samples containing metribuzin up to 2% of sepiolite form a microstructure, which is independent of sepiolite concentration. Addition of metribuzin seemed to weaken the microstructure, and its release behaviour seemed to be related to the microstructure.

The release of metribuzin from the prepared formulations into water was retarded, when compared with the commercial formulation, except in the case of G28. These results were in accordance with those from soil column experiments where the G28 and the commercial formulation eluted almost completely after 4 pore volumes. On the contrary, the total leaching percentages of the other gel-clay based formulations were about half of the total applied amount. An extraction of the active ingredient along these soil columns showed a larger amount in the upper part of the soil column which is of prime interest for weed control (Fig. 1). Bioassays performed at different soil depths paralleled those of the extracted amounts showing a high herbicidal activity in the 0-8 cm depth.

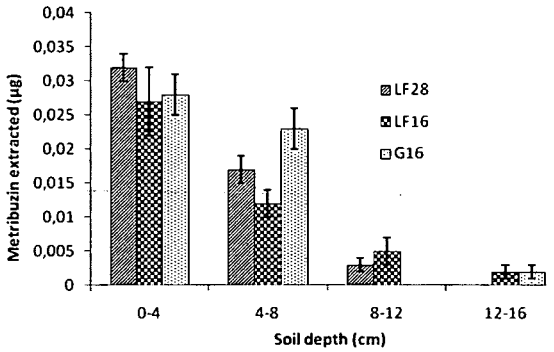

Fig. 1: Metribuzin residues extracted at different depths of the soil columns.

Hydration thermodynamics of SWy-1 montmorillonite saturated with alkali and alkaline-earth cations

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In the context of using clayey barriers, such as in the disposal of radioactive waste within clayey formations, the assessment of the long-term behavior of the clay materials by geochemical modeling requires a perfect knowledge of their thermodynamic properties. The "Thermochimie" database, created by ANDRA in 1996, provides coherent thermodynamic data sets for many minerals of interests, including clay minerals. However, the thermodynamic properties of clay minerals, which govern their stability in solution, are still poorly understood and few experimental data of hydration are available for smectites. A set of consistent data of hydration is proposed from numerous measurements of enthalpy of immersion, and isotherms of adsorption – desorption for SWy-1 montmorillonite saturated with alkali and alkaline-earth cations. To retrieve standard state thermodynamic properties for smectite hydration and dehydration from such data, the amount of H_2O in excess of that located in the interlayer space must be assessed and subtracted from the total amount taken up by the clay sample. Careful measurements of water uptake and release during the hydration and dehydration of the SWy-1 montmorillonite have therefore been taken into account [1,2].

Considering the following reaction: Smectite n_m H_2O = Smectite (0 H_2O) + n_m H_2O (l), the hydration of smectite is calculated by assuming a regular solid solution involving anhydrous and hydrous components in which n_m is the maximal number of moles of water in the fully hydrated end-member [3]. Paired hydration and dehydration isotherms in the one hand and enthalpy of immersion in the other hand, which characterize the equilibrium between water and smectite, can be regressed to assess standard state thermodynamic parameters (enthalpy and entropy) for the hydration - dehydration process.

Validation of standard state thermodynamic properties of hydration of the end members has been achieved by (1) comparing the behavior of hydration-dehydration with experimental measurements done on hetero-ionic SWy-1 and homo-ionic SWy-1 samples at different temperatures; (2) comparing experimental integral enthalpy and entropy of hydration of SWy1 samples with calculated values; and (3) comparing results with those obtained for various smectites with different layer charges (Upton, MX80).

The developed and validated model can predict the standard state thermodynamic properties of hydration and the number of moles of interlayer water in smectites for a given temperature and relative humidity. It may help solving many questions like: the mechanism of exchange between two cations, the number of moles of water transferred during exchange for a given temperature, and the cation selectivity at a given relative humidity. When a limited number of measurements are available, the predictive model can be applied to different compositions to provide theoretical thermodynamic values of formation for hydrated smectites and calibrated with measured data from the literature or acquired within the framework of the project.

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Photocatalytic degradation of Rhodamine B in water by synthetic Zn-substituted phyllosilicates

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Nanolayer has been paid attentions as building block for novel photonic, electronic, environmental, and energy-related materials. Phyllosilicates are abundant in nature, and are layered materials that contain two-dimensional metal octahedral sheet and silica tetrahedral sheet. In another point of view, phyllosilicates are considered to be the self-assembled silicate nanolayers of octahedral and tetrahedral sheets. Phyllosilicates containing transition metal ions can be used for specific catalytic applications. In the present work, we have demonstrated the photocatalytic activity of Zn-substituted phyllosilicates (smectite, vermiculite and mica) which synthesized by "adaptation of processes in the formation of natural geologic analogues"; a new concept called Geonics [1].

The decomposition of organic dye, Rhodamine B (RhB) in aqueous suspensions of the synthetic Zn-substituted phyllosilicates, Zn-saponite and Zn-hectorite, Zn-vermiculite, Zn-mica and rutile under ultraviolet light illumination were monitored with a UV-visible absorption spectroscopy. In aqueous solution with Zn-smectites, the reduction of peak absorbance for RhB was observed in the adsorption spectra, although the shape and the width of their absorption bands were similar to that in aqueous solution. This adsorption behavior indicated that RhB molecules adsorbed onto the surface of Zn-smectites particles without discernible aggregation and the adsorbed RhB molecules were well dispersed. It was confirmed that the hybridization of RhB with the exfoliated Zn-smectites particles enhanced a photodegradation exponentially. On the other hand, Zn-vermiculite and Zn-mica in aqueous solution showed little photodegradation of RhB. The results indicated clearly that the high photocatalytic activity of smectites is attributed to the exfoliation behavior, that is, the nanosheet structure of the synthesized Zn-smectites. Furthermore, the characteristic stability of smectites in aqueous systems in a wide range of pH and redox conditions would make it an ideal nanomaterial in environmental purification.

[1] Yamada, H. et al. (2009) *Trans. Mater. Res. Soc. Jpn.*, **34**, 363-366.

Removal of silica impurities from bentonite by NaOH dissolution

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Bentonites usually contain quartz, α-cristobalite, opal-C, opal-CT, and opal-A as associated silica impurities, which must be removed from bentonites due to the designation of respirable quartz and cristobalite as 'type 1' human carcinogens. These silica impurities could hardly be separated from montmorillonite by conventional wet sedimentation.

In this paper, bentonite was sampled from Xinhe County, Inner Mongolia, China; the mineral composition is as follows: montmorillonite (65.1%), cristobalite (33.0%), and quartz (1.9%). The removal of cristobalite and quartz from bentonite by NaOH dissolution was explored in detail. The result (see Fig. 1 and Fig. 2) shows that the quartz had very different reactivity compared with the cristobalite, only the cristobalite could be separated from montmorillonite by this method.

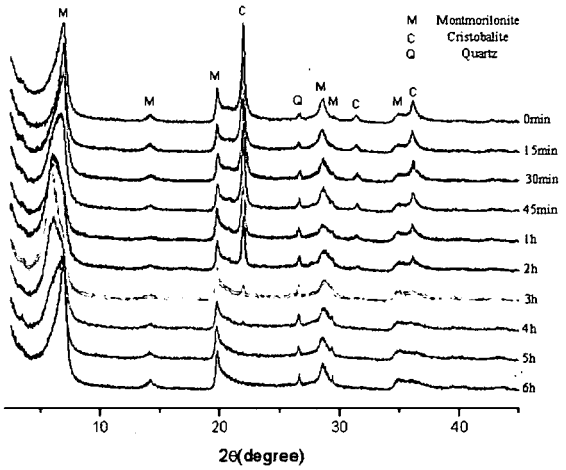

Fig. 1: XRD patterns of the bentonite samples reacted with 0.5 M NaOH at 90 °C with different reaction time.

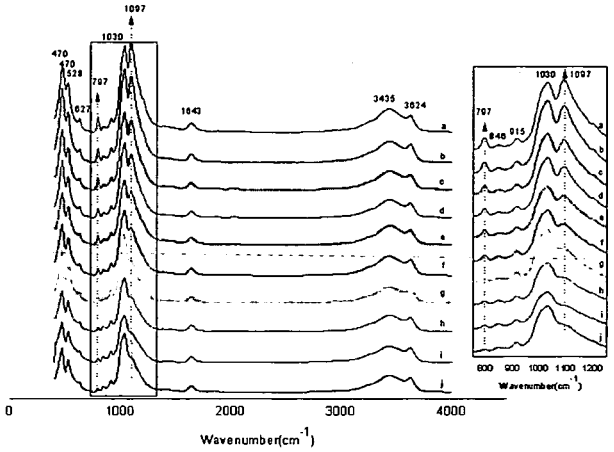

Fig. 2: FTIR spectra of the bentonite samples reacted with 0.5 M NaOH at 90 °C with different reaction time (a-j corresponding 0min-6h).

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Layered minerals nanotopography and surface potential: biomedical and bioengineering applications

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The knowledge of the surface properties of layered minerals is of great importance to understand basic and applied technology, such as, for example liquid/surface interactions, microfluidity, friction or tribology and biomolecules self-assembly and adhesion. Recent developments of Scanning Probe Microscopy (SPM) have widened the spectrum of possible investigations that can be performed at a nanometer-scale level on the surface of minerals. Investigations involve physical properties, such as surface potential and electric-field topological determinations, and chemical and spectroscopic analysis in air, in liquid or in a gaseous environment.

After a brief introduction of new technological developments relating to SPM, recent achievements are presented in characterization and application of nanomorphology and surface potential properties of minerals, in particular the behaviour of some layer silicates. Two general research directions are presented: application of bio/organic surface interactions of layer silicates, and mineral hydrophilicity/phobicity and friction/adhesion issues.

(1) The ability to control the binding of biological and organic molecules to a crystal surface is central in biotechnology, catalysis, molecular microarrays, biosensors and environmental sciences. For instance, recent achievements showed that DNA molecules have different binding affinities and assume different conformations when adsorbed to various layer silicate surfaces. On certain crystals, the electrostatic surface potential anisotropy can order and stretch the DNA filament, thus inducing a natural change in its conformation. The experimental results are in good agreement with simulations and mathematical modeling. The active stretching of DNA on extensive layer silicate surfaces is a clear indication of the potential in understanding basic behavior and developing technological uses of these minerals when used as substrates for biomolecules. Examples involving nucleotides, RNA and cells are presented also.

(2) Investigations of nano-confined adhesive and shear forces of water (and other liquids) onto layer silicate and other mineral surfaces are presented. The study of water in confined geometries is very important because it can provide simple models for nano-bio-tribology and fluid/mineral interactions. Nano-confinement is obtained between a resonating (oscillating) probe and layer mineral surfaces. When the liquid-film thickness is less then a critical value, the oscillation amplitude curve follows a step-like trend, suggesting that the liquid molecules are organized in layers. By using a harmonic oscillator model it is possible to calculate the variation in the elastic and viscous stress response of the confined liquid and to characterise its state respect to the mineral surface.

Montmorillonite as efficient carrier of Gentamicin used for antibiotic treatment: comparison of MD simulations with experiments

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There is a strong demand to identify new strategies in order to set optimal drug delivery systems for antibiotic treatments. Intercalation of organic molecules into layered inorganic solids provides a useful and convenient route to prepare hybrids that show properties of both the inorganic host and organic guest in a single material [1,2]. Both natural and synthetic clays have been already used with success for this purpose. One of the main system widely investigated to modulate drug release, consider smectite clay particles, especially montmorillonite (Fig. 1).

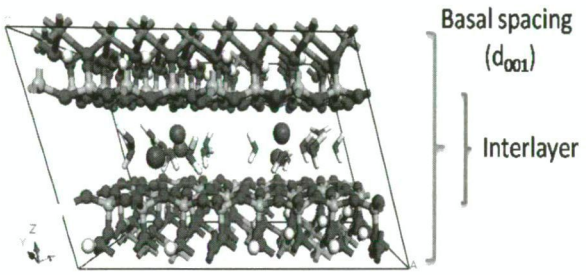

Fig. 1: Ideal model of a Wyoming-type montmorillonite.

High specific surface, adsorptive capacity, rheological properties, chemical inertness and low or null toxicity make clay minerals futuristic drug delivery vehicles [3].The presented work shows the potential of a montmorillonite-based clay mineral (bentonite) to contribute to the development of novel antibiotic materials. In our knowledge, it is the first time the have been tested the intercalation of gentamicin molecules in montmorillonite as a drug delivery carriers for antibiotic treatment (Fig.2).

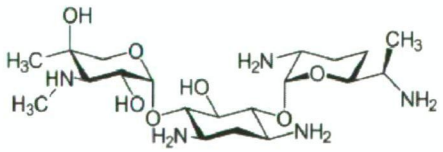

Fig. 2: Gentamicin.

Comparison of experimental measurements (XRD, TGA, DTA) with simulations (MD modelling) have provided a more detailed understanding of the geometry, organization of gentamicin molecules confined in the cationic clay. By MD simulations it has been possible obtain a further insight into the interactions between the organic guest and the clay framework in view to optimize the cationic exchange process.

[1] Mohanambe, L. et al. (2005) *J. Phys. Chem. B*, **109**, 1561-1568. [2] Ghanshyam, V.J. et al. (2009) *Int. J. of Pharm.*, **374**, 53-57. [3] Lin, F.H. et al. (2002) *Biomaterials*, **23**, 1981-1987. [4] Bujdàk, J. et al. (2009) *Envir. Sci. Technol.*, **43**, 6202-6207.

Adsorptive properties of Fe-, Al-, Fe/Al-montmorillonites

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The use of natural sorbents can increase economic efficiency of sorption technologies due to their availability, relative cheapness and the possibility of recycling. Natural montmorillonite (MM) clays are effective cation exchangers. At present, an urgent task remains the development of anion-exchange sorbents, based on montmorillonite. Layer-pillar structured materials synthesized by intercalating metallic polyoxocomplexes between silicate layers of swelling clays, such as montmorillonites attract the interest as sorbents. Fe-, Al- and Fe/Al-montmorillonites were prepared from naturally occurring montmorillonite (clay deposit Mukhortala, Russia) by exchanging interlayer cations (Mg^{2+}, Na^{+}, K^{+}) with polyoxocations containing a) iron (Fe-MM), b) iron and aluminium within the complex with Fe/Al = 1:1 (Fe/Al-MM), c) $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Al-MM). The synthesized solids were calcined for 2 h at 400°C, 500°C and characterized by IR-spectroscopy, XRD, chemical analysis and BET surface area measurements.

The cation and anion exchanging properties of solids were studied in aqueous solutions using as adsorbates cationic (Methylene blue (MB)) and anionic (Acid chrome blue-black (ACBB), Congo red (CR)) organic dyes, NH4+, phosphate, chloride ions and anionic surfactants (Sodium dodecylsulphate and Sulphonole). An intercalation MM by Al, Fe and Fe / Al-polyoxocations reduces the cation exchange capacity (CEC) of ammonium cations and adsorption capacity (AC) of the cationic dye MB in comparison with natural MM. Adsorption of dye MB on studied sorbents depends not only on the number of cation-exchange centers, but also on the size of their accessible surface. Value of adsorption on the sorbents decreases in the series: Fe-MM> Fe/Al-MM> Al-MM, which corresponds to the decrease of the total surface area of meso- and macropores. Introduction of Al, Fe and Fe/Al-polyoxocations to the structure of MM leads to a significant increase in the adsorption properties with respect to anions (chloride, phosphate), due to an increase in the number of anion-exchange centers. Results on the adsorption of anionic surfactants also confirm the increase in anion-exchange capacity of MM for intercalation. Adsorption capacity of phosphate decreases in the series: Al-MM> Fe-MM> Fe/Al-MM> Natural MM, which corresponds to a change in the total specific surface of these sorbents, indicating the accessibility of micropores for adsorption of phosphates. Adsorption capacity for anions of organic dyes for sorbents were subjected to heat treatment at temperatures $\leq$ 300 °C, correlates with the number of anion-exchange centers and the total surface area. Calcining at temperatures $\geq$ 400 °C leads to a decrease in accessible pores surface for microporous adsorbent Al-MM and reduction of AC for large organic anions, whereas the adsorption of inorganic anions remains high and 3-6 times higher than AC for natural MM. Increasing the size of sorbed anions and their degree of association in aqueous solutions leads to a decrease in AC by steric factors, as was observed for the large anions of dyes ACBB and CR. Microporous sorbent Al-MM is effective for removal from aqueous solutions of inorganic anions, and for the removal of large organic anions are effective Fe-MM, Fe/Al-MM having mesoporous structure.

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ACE anionic inhibitors-clay nanocomposites: synthesis and characterization

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ACE inhibitors are used for controlling blood pressure, treating heart failure, preventing strokes, and preventing kidney damage to people with hypertension or diabetes. In the present study, the selected drug for loading onto the layered matrix was captopril (Fig. 1).

Layered double hydroxides (LDHs), also called hydrotalcite-type anionic clays, consist of cationic brucite-like layers and exchangeable interlayer anions [1]. Due to their biocompatibility, some LDHs having different cationic pairs, such as Mg/Al, Zn/Al, Fe/Al or Li/Al-LDH, can be used as host materials for drugs in order to obtain LDH host–guest supramolecular structures [2, 3].

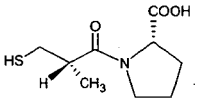

Fig. 1: The chemical structure of captopril, (*2S*)-1-[(*2S*)-2-methyl-3-sulfanylpropanoyl]pyrrolidine-2-carboxylic acid.

Calcined layered double oxide precursor (MgAl–LDO) used for intercalation was obtained by calcination of the layered double hydroxide containing Mg and Al (MgAl–LDH) at 500°C for 2h. Then, the calcined product was re-hydrated in the presence of a captopril solution under a N_2 atmosphere. The obtained material was analyzed by N_2 sorption, UV-vis DR and FTIR Spectroscopy methods.

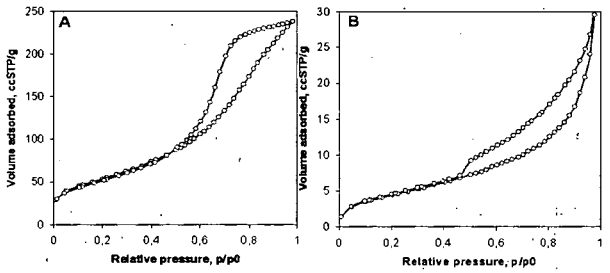

Fig. 2. The N_2 adsorption/desorption of (A) MgAl-LDO and (B) Captopril-MgAl-LDH.

The N_2 adsorption isotherms (Fig. 2) showed that the captopril molecules are successfully loaded into the layered matrix. The specific surface area and the pore volume decrease significantly after the drug loading (Table 1).

Table 1: Textural properties of the studied samples

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)
MgAl-LDO	195.5	0.3571
Captopril-MgAl-LDH	16.2	0.0371

The FTIR and UV-vis DR spectra show the presence of the absorption bands characteristic to the organic captopril molecules. The present study may offer broad perspectives in utilizing MgAl-layered double hydroxides as an alternative biocompatible inorganic matrix for a feasible drug reservoir or a drug delivery carrier.

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Effect of microbiological activity on the flow/rheologic properties of aqueous kaolin mineral suspensions

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The aim of the present study was to investigate the rheologic properties of different type of kaolin infected by microorganisms.

Microorganisms are widespread in the different environmental systems, such as air, water and soil. However, interactions between industrial raw materials and microorganisms are not investigated in details [1]. It was found that these industrial raw materials (different type of kaolin) provide appropriate conditions for microorganisms especially sulfate reducing bacteria. Organic and inorganic compounds of kaolin can serve as nutrition source for microorganisms, accordingly of lignite for fungi and metals for specific bacteria. The organic additives (e.g. regulator substances, hydraulic oil, machine oil) that facilitate the processing serve as additional nutrition sources. Temperature, moisture and nutrition play a key role in the reproduction of microorganisms. Each long-term process involves the danger of proliferation of microorganisms, which phenomenon has an effect on the rheologic properties of kaolin suspensions. 30-40°C temperature for a long time had been creating ideal conditions for proliferation of microorganism, which caused drastic changes in the rheologic properties of kaolin samples. We investigated the rheologic changes of infected and uninfected kaolin samples depended on temperature. According to our results, sulfate reducing bacteria influenced significantly the rheologic properties of kaolin.

[1] Heimstädt, K.H & Mörtel, H.M. (1995) *Ceramic Forum Int.*, **72(9)**, 546-550.

Water uptake and mucoadhesion of chitosan/montmorillonite composite

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Naturally occurring clays and clay minerals may be suitable to effectively modulate drug release. However, sometimes it is necessary to use modified or synthetic clay minerals and/or polymeric additives [1]. Clays and biopolymers have been proposed as interesting materials for new drug delivery systems [2]. Chitosan, a polymer derived from chitin used as a pharmaceutical excipient [3], have been added to montmorillonite dispersions to modify rheological properties related to flocculation state of the resultant dispersions [4]. Chitosan has been also proposed to be used in colon-specific drug delivery systems as regards of its degradation by colonic bacteria [5]. However, due to its high solubility and swelling properties in acidic media, chitosan alone is unable to prevent drug release in the stomach and small intestine, being desirable to get some strategies to avoid such problems. In particular, synthesis of composites with clay minerals may be a novel approach to modify swelling and water uptake of polysaccharides [6]

With these premises, biocomposites between chitosan base (CS) and a commercial montmorillonite (Veegum HS©, VHS) have been prepared by solid-liquid interaction and the water uptake profiles in acidic environment and mucoadhesive properties evaluated, in comparison with the single components. Water uptake measures were done by using a modified Enslin apparatus [7]. Mucoadhesive properties were investigated with a TA-XT2 Plus Texture Analyser (Stable Micro Systems, Enco, Italy) using porcine gastric mucin as biological substrate.

The CS/VHS composites showed lower solubility than pure chitosan in acidic environment and mucoadhesión followed the trend CS > CS/VHS > VHS. It can be concluded that the interaction between the clay particles and polymer chains results in a composite with good mucoadhesive properties, and promising solubility pattern to be used as colonic delivery excipient.

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Iron-clay-bacteria interactions in quartz sands purification

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Several natural sands are brown for the presence of iron and clay minerals that coat or which are impregnated on quartz grain surfaces. *In-situ* washing and bioleaching processes can remove iron and clay minerals.

The following mineral composition (wt %) of the different grain sizes was obtained using Rock Jock software: 31 % quartz, 11 % K-feldspar, 15 % plagioclase, 20 % mica, 11 % kaolinite and 12 % chlorite in the fraction 0.002-0.063 mm and 15 % quartz, 8 % K-feldspar, 4 % plagioclase, 28 % mica, 19 % kaolinite and 26 % chlorite in the grain size fraction < 0.002 mm. Iron-clay-bacteria interaction was found during a laboratory bioleaching of separated iron-clay fraction. The impoverishment by fine-grained fraction is a result of bacterial destruction of silicate minerals. After bioleaching the amount of the fraction 0.9 - 25 μm μm decreased, on the other hand the distribution of the coarse-grained fraction with particle size from 25 to 87 μm increased in the clay sample.

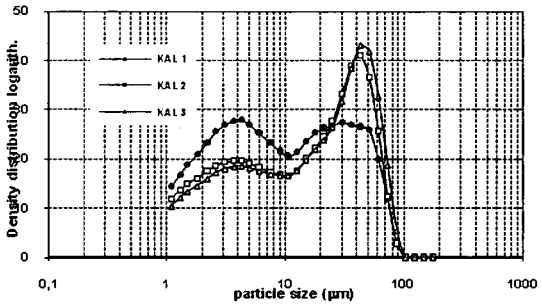

Fig. 1: Granulometric analysis of the clay fraction before (KAL 1) and after bioleaching (KAL2 – *Bacillus* spp., KAL3 – indigenous bacteria).

Dissolved Fe amount under pH ranging between 4 and 7 and in a nutrient-rich environment simulating the conditions of an *in-situ* quartz sands purification, was periodically monitored for 30 days. Mössbauer spectroscopy was used to detect the present iron cations in the natural sample (KAL 1); experimental data indicated that Fe^{3+} cations in KAL 1 can be ascribed to a ferrihydrite-like phase. In *Bacillus* spp., and indigenous bacteria treated samples (KAL 2 and KAL 3, respectively) Fe^{3+} was prior removed always from the same position and, in addition, higher Fe^{3+} decrease was obtained for sample KAL 2.

Table 1: Chemical composition of the clay fraction before (KAL 1) and after bioleaching (KAL2 – *Bacillus* spp., KAL3 – indigenous bacteria)

Elements (%)	KAL 1	KAL 2	KAL 3
SiO_2	56.9	57.5	57.3
Al_2O_3	18.5	18.1	18.5
Fe_2O_3	7.04	4.42	4.65
TiO_2	0.44	0.44	0.45
CaO	1.27	0.90	0.85
MgO	0.92	0.80	0.79
Na_2O	1.19	1.34	1.35
K_2O	2.01	2.33	2.38

The effect of iron-bacteria complexation by exudates caused the clay dissolution with the release of silica. Bacterial clay dissolution liberated iron to promote quartz sands purification.

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Selection of protein amino acids in natural montmorillonite gel

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At the studies of biomineral interactions the natural montmorillonite gels from mineral deposits provide the most versatile information on the real environments and processes of synthesis of nucleotides and other biomolecules.

We studied gel accumulations from hydrothermal fluorite deposit Palat in Bulgaria, where in 1983 the gel samples were selected and hermetically packed. The material of preserved and fresh samples is completely identical by their composition and properties.

The gel represents homogeneous jelly-like snow-white mass. The dispersed phase are two-dimensional (length 15 mcm, width 0.4-0.8 mcm) thin-banded individuals of Ca, Mg-montmorillonite, the dispersion medium-strongly mineralized water of chloride-sulphate-bicarbonate calcium-natrium composition.

The electronic microscopy studies of fresh or not long preserved (one-two years) samples of gel-montmorillonite showed numerous rod-like bacteria. In the long preserved gel living bacteria were not observed, however SEM studies showed bacterium-like forms of Cu-Fe-Zn composition without sulphur, which probable represent brass pseudomorphoses on fossilized bacteria.

The gel-montmorillonite contains 0.28% $C_{org.}$ Chromato-mass-spectrometry of organic matter extract from the montmorillonite testifies to its peculiar composition. The group of acyclic alkans and alkens are the most interesting, which are distinguished by the isomerism of carbon framework and position of multiple bonds. There is also a number of aromatic and heterocompounds. Such a composition of organic compounds is not characteristic for hydrocarbons (of geological nature), and seems to be consequence of montmorillonite selection. At the end of the chromatogram there are C_{26}-C_{35} n-alkans, which are typical components of petroleum series.

In the natural gel-montmorillonite the presence of a wide spectrum of amino acids (Glu, Gly, Ala, Val, Leu, Tyr, Phe, His, Lys, Arg) has been determined, which considerably differs from the corresponding spectra of sedimentary montmorillonite clays and is closer to the amino acid composition of abiogenous hydrocarbon ordered structures. It is not excluded that the formation of the amino acids results from catalytic action of montmorillonite to the structural transformation of the organic matter of mineral-forming solutions. In 12 years the total content of amino acids decreased by 5 times (from 8.9 to 1.72 mg/100 g of matter). The qualitative composition of the amino acids is practically the same, excluding tyrosine, which is not determined in the primary preservative even in trace quantities. All the amino acids, identified after 12 year-preservation, are represented exclusively by L-enantiomers; D-amino acids were not determined. It is quite reasonable that for the period between two studies the montmorillonite continued to directly select protein amino acids, and the complete chiral selection of left enantiomers passed.

Thus, the peculiarities of structural evolution of montmorillonite gel and its interaction with organic matter allow using the natural gel-montmorillonite both for simulation of possible environments of biomolecular formation and more complex protobiological structures, and as simulations of some biological processes responsible for transfer and transformation of information and feedback

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A thermal analysis study of chromium oxyhydroxide nanoplates synthesised under different pH conditions

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As a transition metal oxide, chromia (Cr_2O_3) has attracted special attention because of its importance in specific applications, such as in high-temperature resistant materials, solar energy collectors, catalyst, and so on [1]. Chromium oxyhydroxide CrO(OH) is a principal precursor for chromium oxides Cr_2O_3, since the original size and morphology of CrO(OH) precursor can be retained after calcination. Three naturally occurring chromium oxyhydroxides are bracewellite (orthorhombic CrO(OH)), guyanite (orthorhombic CrO(OH)) and grimaldiite (trigonal CrO(OH)) [2]. Nanoscaled grimaldiite material has been successfully synthesised in different pH environments through a simple hydrothermal route. Plate-like CrO(OH) crystals with average diameter of 11 nm were observed from transmission electron microscopy (TEM). Thermogravimetric analysis [3,4] was applied to study the thermal decomposition process for the synthesis CrO(OH) nanomaterials (Table 1). The thermal properties of CrO(OH) nanomaterials and the influence of pH to the crystal growth was deduced from this thermal study.

Table 1: Summary of peaks shown in dTG curves for CrO(OH) nanomaterials synthesised in various pH conditions

CrO(OH)-5.0	*CrO(OH)-5.0*	*CrO(OH)-10.0*
45°C, 84°C, 109°C	45°C, 84°C, 109°C	50°C, 80°C
	276°C	238°C
315°C		318°C
	396°C	
444°C, 463°C	438°C	436°C, 458°C
	643°C	

The thermal gravimetric study indicated that synthesised CrO(OH) nanomaterials decomposed at ~ 450°C (Fig. 1). All products after heated to 1000°C were well crystalline Cr_2O_3 nanomaterials, which were confirmed by X-ray diffraction (XRD).

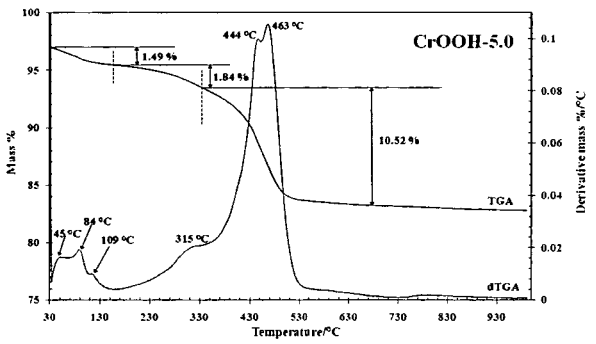

Fig. 1: Thermalgravimetric analysis (TGA) of CrO(OH) nanomaterials synthesised at pH=5.0.

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Cr-rich alunite nodules in acid sulfate alteration zones overlying bentonites at Milos, Greece: evidence for Cr transport by acidic fluids

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Nodular alunite concretions occur at the base of acid sulfate alteration zones in Upper Pliocene to Middle Pleistocene pyroclastic rocks overlying bentonites at Siskinos and Aspro Chorio, Milos, Greece. The white concretions with diameters of up to 50 cm consist of euhedral to partly corroded alunite crystals (1-3 μm, 89-99 vol.%) with minor amounts of halloysite, opal-A, and quartz. The alunites at Siskonos, SE Milos, are characterized by intermediate atomic Na/(Na+K) ratios (0.43-0.73) and high Cr (840-1250 ppm), V (240-580 ppm), moderate Sr (520-650 ppm) and Ba (300-730 ppm) and low Zn (<5 ppm) contents. In contrast, an alunite nodule from Aspro Chorio in the NW of Milos has a very low atomic Na/(Na+K) ratio (~ 0.16) and no detectable Cr (<5 ppm), but high Ba (2580 ppm) and Zn content (140 ppm).

Selective leaching experiments using sulfuric acid and ammonia show that Cr in nodules from Siskinos is not adsorbed to clays and not present as discrete chromite, but most probably located in the alunite crystals. EXAFS studies indicate that all Cr is present in a trivalent state. The calculated Cr-O distance is 1.965Å, which is consistent with an octahedral coordination. The Cr in alunites cannot be derived from the andesitic to dacitic protoliths (<20 ppm Cr [1]), but must have been introduced by hydrothermal sulfate-rich fluids. We suggest that Cr was leached by strongly acidic fluids from ultramafic/mafic rocks in the metamorphosed accretionary wedge in the SE part of the island. We note that steam condensates with a pH 1.7 and temperatures of 90°C at Paleochori Bay, SE Milos, contain up to 3.0 μM Cr [2]. The low Cr contents in alunites at Aspro Chorio in the NW part of Milos are probably related to the absence of ultramafic bodies in the basement. The tabular acid-sulfate alteration zones at Siskinos require input of magmatic fluids. Preliminary stable S, O, H, isotope data of alunites are consistent with this interpretation.

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Relationship between clay mineralogy, fluid inclusions and K/Ar ages in the Triassic and Palaeogene hydrothermal alteration zones within the Variscan granite of the Velence Mts. (W-Hungary)

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The Variscan (Carboniferous) granite intrusion of the Velence Mountains (W-Hungary) has suffered intense argillic alteration in several zones. To determine the structural, temporal and spatial relationship, as well as the p-T conditions of the hydrothermal systems responsible for alterations, a detailed study of the hydrothermal clay mineral assemblages and mineralogical properties of clay minerals has been completed. The idea was that clay mineral assemblages as well as clay mineral properties (e.g. illite structure, kandite minerals) in hydrothermal alteration zones are useful for temperature estimation. Temperatures were compared with the results of fluid inclusion studies and were used as independent thermometers for pressure estimation. K/Ar radiometric age dating was performed on the illite phase to determine the temporal relationship of the alterations. Comparison of clay mineral assemblages, clay mineralogy, fluid inclusion data and K/Ar radiometric dates suggests that the superimposing hydrothermal alterations can be distributed in three groups:

1) Argillic alteration around the quartz-fluorite-base metal veins is composed of illite-kaolinite and smectite clay mineral assemblage and is regionally characteristic for the granite. Intensity of alteration increases towards to the mineralized NE-SW trending structural zones and towards the quartz-fluorite-base metal veins. Age of this type of alteration and thus of the syngenetic base metal veins is middle-late Triassic according to the results of K/Ar age measurements. Field evidence and mineralogical analysis prove that the clay mineral suites did not form simultaneously. Comparing the fluid inclusion data with the clay mineral thermometer the fluids started to cool down from 220°C at relatively low pressure (1 kbar). Cooling was accompanied by dilution of the hydrothermal fluids.

2) Alteration zones of Palaeogene age in the granite evolved in structurally controlled narrow zones in the eastern part of the granite, in the vicinity of Palaeogene subvolcanic andesite dikes cutting the granite. Alteration can be characterized by well-crystallized illite, thin quartz-stringers and silicification. Structural characteristics of illite indicates temperature of at least 220°C in accordance with the fluid inclusion data, measured on fluid inclusions trapped from a shallow level boiling hydrothermal system. K/Ar ages for illite scatter in a narrow time range between 29 and 32 Ma, indicating early-Oligocene age for the hydrothermal system, as well as for the andesitic magmatism.

3) In the broader vicinity of the illitic alteration zones, but also structurally related Palaeogene andesite dykes, illite and dickite were found. Their assemblage indicates 200-220°C temperature but a characteristic fluid inclusion assemblage cannot be connected to this alteration type. Radiometric ages vary in a very broad range between 200 and 50 Ma, depending on the location and the measured sample. Therefore it is assumed that this assemblage does not represent a third, individual hydrothermal event but can be interpreted as a transitional zone between the Triassic and the Palaeogene alteration zones.

Alpine (Cretaceous) very low- to low-grade metamorphism recorded on illite fraction from South Tisia (eastern Mt. Papuk, Croatia)

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Alpine very low- to low-grade metamorphism related to Cretaceous orogenesis has been investigated in the Slavonian Mts., Croatia. Samples belonging to the Psunj metamorphic complex (PMC), Radlovac metamorphic complex (RMC) and clastic-carbonate succession of the Late Permian to Early Triassic age i.e. Permian-Triassic sedimentary sequences (PTSS) were studied.

Kübler and Árkai indices of all analysed samples indicate high temperature anchizonal to epizonal conditions of thermal alteration (~300°C). The degree of thermal alteration tends to be constant in all measured samples implying that different complexes passed through and recorded the same event. Measurements of b_0-parametar of samples belonging to the RMC imply transitional low-medium pressure metamorphism. K-Ar ages measured on <2 μm fraction indicate Late Cretaceous very low-grade metamorphism of PTSS as well as Late Cretaceous overprint of older Paleozoic metamorphic rocks (PMC and RMC). No considerable systematic or gradual variation between the K-Ar age of <2 μm fraction and metamorphic indicators of analysed samples, regardless to the stratigraphy, was observed (Fig. 1).

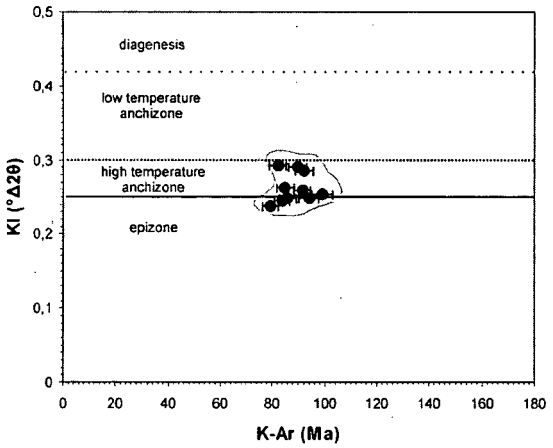

Fig. 1: Plot of KI values vs. K-Ar ages of <2 μm fraction.

All these data together with K-Ar ages measured on <2 μm fraction point to Late Cretaceous very low- to low-grade regional metamorphism related to the Austrian and/or Subhercynian phase of Alpine orogeny that were responsible for the main nappe-forming compressional events in the Pannonian Basin area and the Carpathians [1].

Metamorphic and geochronological evolution of the studied area is in good agreement with similar scenario for the surrounding area of Tisia, but also from ALCAPA (e.g. [2]).

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The Arosa zone in Eastern Switzerland, the diagenetic to metamorphic pattern of a tectono-metamorphic mélange

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In the area of Arosa-Davos-Klosters (Eastern Switzerland) the different tectonic elements of the Arosa zone mélange e.g. the Austroalpine fragments, the mafic and ultramafic basement rocks as well as the matrix (oceanic sediments and flysch rocks) show a distinctively different metamorphic history and also a different climax („peak") of alpine metamorphism. This is proved by a wealth of Kübler Index (KI) - vitrinite reflectance (VR) measurements and kinetic numerical modelling, bituminite reflectance, illitization indices (related to the smectite-illite reaction progress), K-white mica b-cell dimension determinations, index minerals, microprobe data as well as geo-chronological results.

Whereas the matrix sediments of the Arosa zone mélange are overprinted by a low anchizonal to high anchizonal metamorphism Lower Austroalpine fragments in the mélange and the adjacent Lower Austroalpine units (e.g. Tschirpen-Dorfberg nappe) were overprinted by a widespread syn-sedimentary burial and orogenic epizonal metamorphism. High anchizonal rocks are found in the Lower Austroalpine locally. Flysches at the hanging wall of a disconformity in the mélange zone show lower diagenetic thermal conditions.

At least six main metamorphic events can be recognized in the area of Arosa-Davos-Klosters:

i) A pre-orogenic event is recognized in the sediments at the base of the Silvretta nappe, typical for the Upper Austroalpine.

ii) The epizonal oceanic metamorphism observed in the close vicinity of oceanic basement rocks (e.g. pillow-basalts, peridotites of the South Penninic units) of the Arosa zone is another pre-orogenic process.

iii) Based on stratigraphic, tectonic and geo-chronologic considerations the overprint of lower structural Austroalpine fragments in the Arosa zone and the adjacent Lower Austroalpine nappes is attributed to the orogenic metamorphic processes during the Late Cretaceous.

iv) The thermal climax observed in the sediments of the Arosa zone can be bracketed into the time span between the Austroalpine Late Cretaceous (iii) event and the middle Tertiary event in the Middle Penninic (v) as well as the Oligocene "Turba phase". North of Klosters, in the northern part of our study area, the entire tectonic pile from the North Penninic flysches to the Upper Austroalpine is strongly influenced by a late Tertiary event (vi).

In the Arosa zone mélange an individual orogenic metamorphic event is evidenced and gives a new chance to resolve still not understood diagenetic-metamorphic versus deformation relations. By different KI-VR correlations we can distinguish 6 heating episodes in sedimentary rocks and 7 deformation cycles. This is well explained by the propagation of the Alpine deformation front onto the foreland units.

Origin and timing of brittle shear zones in the Mórágy Granite (Hungary): mineralogy and K-Ar geochronology of illite-rich fault gouges

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The Mórágy Granite — exposed in the south-eastern hilly foreland (Mórágy Hills) of the Mecsek Mts. — represents an Early Carboniferous pluton (~340 Ma) in the Variscan crystalline basement (Tisza unit) of the Pannonian Basin. It is mainly composed of microcline megacryst-bearing biotite-monzogranites with mafic enclaves of predominantly monzonitic composition, hybride rocks and leucocratic dykes crosscutting all of these rocks. Following a Variscan regional metamorphism, during cooling associated with the formation of a regional, generally NW-dipping foliation and localized ductile shear zones, the pluton suffered intense brittle deformation in several phases. During these events — beside micro- and macro-scale individual fractures — numerous, map-scale brittle shear zones were also formed which display a remarkably large variety in orientation, width, internal structure as well as in mineralogical composition.

In this study we focus on the so-called core zone(s) of mature shear zones containing well-developed, partly foliated, brittle fault rocks as fault breccias, cataclasites and clay gouges concentrating the deformation into relatively narrow zone(s). Among them, (foliated) clay fault gouges are of special interest, since these represent not only the most intensively deformed brittle fault rocks, but also the products of syntectonic fluid/rock interaction. The analyzed gouge samples contain illite/smectite + chlorite + palygorskite + kaolinite + quartz + K-feldpar + plagioclase + calcite + dolomite + hematite + goethite assemblage with highly various ratios of the individual minerals. Clay minerals and chlorite are clearly new phases, formed at the expense of feldspars and mafic minerals of the original granitoid protolith. According to detailed XRD analyses, the polytypic variety of illite in clay gouges containing illite in considerable amount is almost exclusively 1M, suggesting hydrothermal origin of illite. In some samples minor amounts (<10 wt%) of $1M_d$ and/or $2M_1$ polytypes also occur. The $1M_d$ polytype may represent the low-T alteration product of the 1M hydrothermal illite, whereas the $2M_1$ polytype presumably display inherited component from primary magmatic biotite and/or metamorphic muscovite. The FWHM (full-width-at-half-maximum) values of 1M illite are mostly higher than 0.73 $\Delta°2\theta$), but another group with significantly lower values (0.51–0.61 $\Delta°2\theta$) is also present. The higher values of the first group probably reflect the mixed-layer structure (illite/smectite) of the analyzed phases and occasionally additional smectite as well, whereas the second group represents a discrete illite structure. K/Ar dating of illite-rich fine fractions (<10, <2, <1 μm) resulted in strongly scattered Mesozoic ages (Middle/Late Triassic–Late Cretaceous). Considering various mineralogical/structural criteria (amount of I/S, smectite, other, „disturbing" phases, as well as the FWHM values), we conclude that the oldest (Triassic–Early Jurassic) and presumably the youngest (Late Cretaceous) ages seem to represent indeed the time of important brittle tectonic activities accompanied with syntectonic fluid flow. The Middle Jurassic and Early Cretaceous ages might also indicate real tectonic events, if one regards the considerable amounts of illite/smectite and smectite in these samples as cogenetic phases with hydrothermal illite (and not as alteration products of it). However, further detailed investigation is needed to verify this hypothesis.

Two types of illite with different chemical composition in Upper Riphean shale, the Zil'merdak Formation (South Urals)

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Precambrian argillaceous rocks often contain mixtures of non-cogenetic illite minerals with different crystallochemical and isotope characteristics. The end-members of these mixtures could be formed at different stages of lithogenesis.

Shale samples were collected from the two sections of the Upper Riphean Zil'merdak Formation (Bakeevo village and Minyar) spaced by 200 km. The <2-μm fractions of these samples were separated into 1-2, 0.6-1, 0.3-0.6, 0.2-0.3 and 0.1-0.2 μm subfractions (SF). SFs were leached with NH_4OAc to remove mobile Sr adsorbed on the surface and located in interlayer positions of clay particles, or incorporated into the soluble accessory minerals such as carbonates and phosphates. SFs were studied by the XRD technique, and concentrations of K, Rb, Sr and the Sr isotope composition were determined in the residues after leaching. All the SFs in both samples are dominated by illite, an admixture of chlorite is no more than 5-10 per cent.

The 0.1-0.2 and 0.2-0.3 μm SFs of the sample from the Bakeevo section contain $1M_d$ illite, the 0.3-0.6 and 0.6-1 μm SFs contain $1M$-$1M_d$ illite. A small admixture of $2M_1$ illite occurs only in coarser SFs (0.6-1 and 1-2 μm). The SFs of the sample from Minyar section also consist of illite. $1M_d$ illite is abundant in finer SFs (0.1-0.2 and 0.2-0.3 μm), whereas 1M illite with some amount of $2M_1$ dominates in coarser SFs (0.3-0.6 and 0.6-1 μm). Illites in all the SFs of both samples have high CIS values (Crystallinity Index Standard) and comply with the zone of diagenesis.

Table 1: XRD and chemical data for fine subfractions of the Zil'merdak shale

SF, μm	CIS	I_{002}/I_{001}	K, %	K/Rb	$^{87}Sr/^{86}Sr$	$^{87}Rb/^{86}Sr$
# Bakeevo						
0.1-0.2	1.63	0.46	6.13	254	1.2039	62.26
0.2-0.3	1.57	0.39	6.20	254	1.1491	52.98
0.3-0.6	1.38	0.36	6.11	243	0.9223	21.54
0.6-1	1.17	0.25	5.50	235	0.8506	11.71
1-2	0.95	0.25	5.15	228	0.8282	8.915
# Minyar						
0.1-0.2	0.92	0.40	5.81	225	1.4653	80.29
0.2-0.3	0.80	0.28	5.93	235	1.3615	67.43
0.3-0.6	0.80	0.36	5.56	234	0.8999	17.73
0.6-1	0.74	0.38	4.65	215	0.8397	9.898
1-2	0.60	0.40	4.21	212	0.7854	5.358

These relationships together with the XRD data suggest that the silicate component in SFs includes a mixture of two possibly non-cogenetic illite end-members with different chemical composition. In addition, the linear alignment of the residue data points for the SFs of different size in both the $^{87}Rb/^{86}Sr$ - $^{87}Sr/^{86}Sr$ and the $1/Sr$ - $^{87}Sr/^{86}Sr$ diagrams provides a convincing proof of the two-component mixing systematics.

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Clay minerals as climatic proxies, possibilities and limitations

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In sedimentary geology, clay minerals have been widely used to reconstruct palaeoclimates as it has been shown that their latitudinal distribution in modern soils depends on climatic conditions. Latitudinal distribution also occurs in marine sediments deposited in oceans, thus allowing clays from old marine sediments to be used for palaeoclimate studies. These include many techniques, the most widely used being the determination of stable isotope ratios measured on carbonates and/or phosphates that give an idea of oceanic temperatures, but few proxies except clay minerals can be used to estimate moisture which is the other main parameter of climate. The combination of stable isotopes and clay mineral studies in very fruitful, as the two main climatic parameters can be associated for the same period.

The interpretation of clay mineral assemblages in terms of climate is possible only if burial diagenesis is negligible, generally when the total burial depth is estimated to be less than 1500m. The occurrence of smectite and/or I/S R0 in the sedimentary successions indicates weak diagenetic influences but additional data on T_{max} measured on organic matter can be very useful to evaluate the diagenetic influences. Practically, in most sedimentary basins it is difficult to identify a reliable climatic signal in sediments older than the Jurassic.

In porous sedimentary rocks (sandstones or dolomites), the occurrence of authigenic clay minerals (kaolinite and chlorite) is common and should be taken into account in the interpretation of clay assemblages. Generally, strong relationships between lithology and clay assemblages reveal the occurrence of authigenic clays.

Palaeoclimatic studies should also be based on many sections originating from different sedimentary basins, because strong differences in clay mineral assemblages are often encountered from one section to another either because of differential settling processes or because of different provenances for clay minerals. Therefore a compilation of clay mineral data originating from coeval sediments is necessary.

Clay minerals must originate from the erosion of weathering profiles contemporaneous to sedimentation. This condition is rarely obtained as clays are often reworked from old sedimentary rocks cropping out on continental areas. Despite all these limitations, we present several examples from Meso-Cenozoic successions showing the possibility of using clay minerals as a palaeoclimatic tool in association with other proxies, but also some examples showing misinterpretations of clay mineral assemblages either because of diagenesis, authigenic processes or reworking from old rocks.

Cretaceous-Paleocene-Eocene sedimentation in Arctic Ocean: results from the clay minerals investigation (IODP-ACEX, 302 data)

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Arctic Ocean's influence on the Earth climate is difficult to underestimate. Evolution of climatic periods of the planet is encrypted in the sedimentary section of the Ocean and can be reconstructed through a detailed study of the sediments composition. Present work is based on the materials obtained from the ACEX-IODP Leg 302 drilling on the Lomonosov Ridge, Central Arctic Ocean. Clay fraction of the Campanian, Paleocene and Eocene sediments sampled from the depths of 200-400 m below sea floor was studied with the following methods: X-ray diffraction of bulk and clay samples, scanning electron microscopy, infrared spectroscopy in the near and medium field, and thermal analysis. Based on these data, as well as published data on paleontology and stratigraphy [1,2], it is possible to study the history of the basin development in the Cretaceous-Paleocene-Eocene time including the Paleocene-Eocene Thermal Maximum (PETM), Early Eocene Climate Optimum (EOCO) and Eocene Thermal Maximum (ETM2). Each of these events, as well as the intervals between them are characterized by various associations of clay minerals and the amount of amorphous silica of different origins and different characteristics of clay minerals structure and morphology, which are interpreted as results of different conditions of weathering and transport. Based on experimental data and published materials [2,3], 7 major stages of sedimentary basin evolution in Cretaceous-Paleocene-Eocene time were distinguished:

1. Around 80 Ma (Campanian) – illite-kaolinite association, transport and deposition of material from the water flow of high density – neritic warm humid conditions. 2. ~55 Ma – PETM – smectite association, traces of transportation of sedimentary material, shallow warm basin. 3. ~ 53 Ma – ETM2 – kaolinite-chlorite-illite association, kaolinitization. 4. ~ 52 Ma – EOCO – illite-smectite association, the content of clay minerals not more than 5-10%, large-scale processes desilication, amorphous silica dominant in sediments – continental (probably soil) conditions in a warm climate. 5. ~ 49 Ma – Azola phase – smectite formation in shallow fresh water channels – continental conditions. 6. ~ 46.5 Ma – Early-Mid Eocene Cooling – smectite-illite association, the content of clay minerals 10-30%, the biogenic silica dominant. 7. ~ 44.5 Ma – high variation of clay minerals, due to drastic changes in the supply of terrigenous clay material under the seasonal ice conditions.

After that surface of Lomonosov Ridge was raised and information about sediments period from 44.5 till 22 Ma was lost.

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Clays and authigenic minerals composition on the glacigenic and bedrock contact zone

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Origin of authigenic minerals in the Pleistocene and modern glacigenic and underlying sediments over the world is known and studied long time. Many scientists (e.g. Lavrushin & Golubiev [1], van der Meer et al. [2]) relate formation of the authigenic minerals in the glacial environment to glacial dynamics, bed material deformations and water implication on the sediments. New formed minerals in these conditions on the sediments contact zones are considered as sensitive paleo-environmental indicators.

Aim of this study was clarify possible authigenic minerals in tills from Latvia for future paleoenvironmental reconstructions. Four geological sections in Latvia were analyzed in details. The study sites are situated on the different last glaciation implication zones – the eastern, western and central parts of Latvia and all selected sites has real and visible recognizable contact zone.

Glacigenic (Weichselian) and underlying illitic clayey (Upper Devonian and Upper Pleistocene glaciolacustrine) sediments were analyzed with x-ray powder diffraction (XRD) method. Clay mineral diagnostic was performed on textured samples with chemical treatment, but untextured samples were used for quantitative analysis applied by Quanto software. Scanning electron microscopy (SEM) was used to verify identified minerals and their morphological studies.

Besides several authigenic minerals like calcite and gypsum in the clay sized fractions were recognised also primary minerals – quartz, hematite, feldspars, and secondary minerals – calcite, dolomite and clay minerals illite, kaolinite, smectite. The authigenic minerals mostly are found in the < 0.4 μm fraction, because the differences in the mineral composition does not indicate only mechanical material mixing as in the fractions < 2 and < 1 μm. Calcite was recognized in all clay fractions in all samples from the contact zones of studied sediments. Amount of calcite increase in the fractions < 1 μm and < 0.4 μm, but in the fraction < 2 μm variety was insignificant. The calcite amount increases until 16% in samples which were taken 15 cm above the sediments contact zone. Gypsum amount increase on the sediments contact zone was recognized in fraction < 0.4 μm in the geological section from the western part of Latvia. Clay mineral composition is different between studied geological sections and those variations at the section are not systematically, just illite quantity decrease with authigenic minerals increase in the < 0.4 μm fraction.

Observed calcite and gypsum amount increase in the clayey bedrocks and till contact zone can be explained with settling in the subglacial conditions or with groundwater activity in the postsedimentation time.

Acknowledgements: This work has been supported by the European Social Fund within the project „Support for the implementation of doctoral studies at Latvia University".

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The influence of allophane and palagonite appearance on the unfrozen water content in the frozen volcanic ashes

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Kamchatka and Iceland are the subject areas of very few geocryological studies. All the physical and mechanical properties of the frozen grounds and most of geocryological processes in the cryolithozone are predetermined by the unfrozen water content.

Volcanic ashes of different ages and compositions have been collected from the Kluchevskaya volcano group in Kamchatka (№1-8) and in the south of Iceland (№9). Ash samples had different ages (Table 1).

Unfrozen water content (W_w, %) in the Kamchatka ashes (at -5°C) is change from 0 to 11%; and in the Iceland ash it is 3.5 % [1]. Hygroscopic water (W_g, %) is different for all samples too (table 1).

The unfrozen water content in the studied ashes is connected with the transformation of volcanic glass and the appearance of clay minerals that is presumably controlled by the duration of alteration.

The samples were analyzed by IR-spectroscopy (IR-Fourier spectrometer FSM-1201) in order to determine their mineralogical composition [2]. As results, it was found that the sample № 1 was the waterless allophone, the samples № 2, 5, 6, 7 – were opal, № 3, 4, 8 – were allophanes with the various water contents and the sample № 5 – palagonite [3].

The thermal behavior of the allophanes and the palagonite was studied by DTA and TGA techniques on a Q-1500 D derivatograph (Hungary). The thermal study showed that the mass (W_{term}, %) loss depends directly on the ages of the investigated samples (Table 1).

Table 1: The results of water studies in the volcanic ashes

№	W_{term}* %	Age, years	Glass composition	W_g* %	W_w* %
1	0	35	waterless	0	0
3	3.8	1500	allophane	1.24	2
4	6.2	2000	allophane	4.3	10
8	16.8	8500 –9000	allophane	7.3	10
2	0.6	35	opal	0	0
5	3.1	2500	opal	1	1.1
6	4.4	7000	opal	1.32	2
7	6.7	7000	opal	2.52	3
9	11.6	15000-150000	palagonite	4.71	3.5

*Comment: W_{term} – the water amount, mass. %; W_g, W_w – accordingly the gyroscopic humidity and humidity that conform to unfrozen water content (with respect to dry ground mass), %

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Geochemistry of the hydrothermal dickite from Jedlina Zdroj (Lower Silesia, Poland): Fe^{3+}

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Geochemical analysis for Fe has been made on a representative sample of the dickite-rich hydrothermal clay from Jedlina Zdroj. The mineralogy of the sample is comparatively simple, dickite being the principal component (>90 wt% of total sample), with lesser amounts of goethite and barite. Inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements of the products of subsequent chemical treatments indicate that most of Fe (ca. 97 wt% of total metal) reside in the dickite (Table 1). Electron spin resonance shows that a part of Fe in the dickite structure is in the form of Fe^{3+} ions. A substantial part of these ions (as well as of Fe in the dickite matrix) was probably contained in the original hydrothermal dickite-forming solution.

Table 1: Geochemical concentrations of Fe [ppm][a] in Jedlina Zdroj dickite sample from selective leaching experiments

Fraction	Sediment (±5 wt%)	Fe (ppm)
Acetate buffer	2.0	≤1[b]
Cold-HCl	5.0	3750
Boiling-HCl	2.0	5200
Dickite	91.5	1900
Insoluble residue	0.0	-
Total sample	100.5	2030[c]

[a]Determined by ICP-OES. [b]Detection limit of ICP-OES employed. [c]Obtained by summation of fractional Fe concentrations.

From geochemistry of Fe^{3+}, it is deduced that the oxidation potential (Eh) and H^+ concentration (pH) of the solution during the formation of dickite from the Jedlina Zdroj were approximately >0.45 V (highly oxygenated) and 0-4 (highly acidic), respectively (Fig. 1).

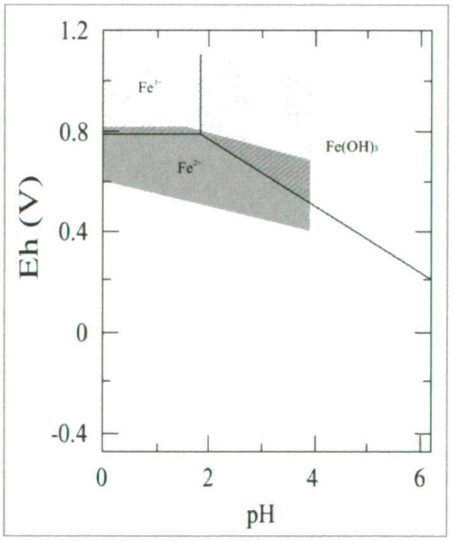

Fig. 1: Eh-pH diagram for iron species in solution at 300 K/1 atm. The assumed total Fe concentration is 200 ppm. The shaded area represents Eh/pH region of the hydrothermal waters [1]. Probable physicochemical conditions of the crystallization of dickite from Jedlina Zdroj are represented by the hatched area.

[1] Kraynov, S.R. & Ryzhenko, B.N. (1992) *Geochem. Int.*, **29**, 1-8.

Hydrothermal kaolin minerals and smectite occurrences in the Gedikler area (Uşak, western Anatolia, Turkey)

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The Gedikler kaolins and coexisting alteration minerals developed within two Pliocene units: the Ahmetler Formation and Beydağı volcanites. The Ahmetler Formation is made up of the Gedikler member, comprising siltstone, claystone and tuffite that formed in a lacustrine enviroment. The Beydağı volcanites, laid down by volcanic activity in the Pliocene, comprise andesitic lava, tuff and agglomerate, which periodically fed the Ahmetler Formation.

These units have been studied via petrography, reflected-light polished-section microscopy, X-ray diffractometry (XRD), differential thermal analysis-thermal gravimetry (DTA-TG), scanning electron microscopy (SEM-EDX), IR spectroscopy (FT-IR) and geochemical analysis. Plagioclase and K-feldspar are argillized, feldspar is sericitized, biotite and hornblende are opacitized, groundmass is argillized and Fe-oxide/hydroxide phases also developed in the volcanic units.

In Gedikler area, kaolin minerals coexist with illite, smectite, gypsum, barite, quartz, calcite, feldspar, hornblende, dolomite, pyrite and traces of alunite (jarosite locally). Infrared spectral analysis exhibits two peaks at 789 (FeFe-OH) and 430 cm^{-1} (Si-O-Mg), confirming partial substitution of octahedral Al by Fe and by Mg. SEM studies reveal that kaolin occurs as rod-like halloysite and platy kaolinite, and that smectite flakes cover degraded volcanic material. Geochemically, the volcanic rocks plot within the trachyandesite and rhyodacite/dacite fields. SiO_2 contents vary from 43.55 to 66.02%, and Al_2O_3 contents are in the range of 13.12-20.86%. SiO_2/Al_2O_3 ratios decrease from fresh rock samples to pure kaolin samples. High Fe_2O_3 (0.74-14.56%) values indicate alteration and the presence of iron-oxide/hydroxide phases. High K_2O (1.03-5.26%) and lower MgO (0.10-2.28%) values reflect the presence of illite, feldspar and smectite. Na_2O and K_2O, which are highly mobile, are extensively removed from all alteration zones, reflecting plagioclase breakdown. Depletion of Mg suggests the degradation of biotite and hornblende during hydrothermal alteration. All of the samples are enriched in large-ion lithophile elements (LILE) and light rare-earth elements (LREE), and depleted in high-field-strength elements (HFSE) and heavy rare-earth elements (HREE) with respect to primitive mantle and chondrite, and are characterized by distinct negative Eu anomalies. These geochemical signatures reflect fractional crystallization and alteration of feldspar.

Clay mineralogy of the hydrothermal alteration around Sındırgı, Balıkesir, Turkey

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Hydrothermal alteration hosted by Miocene calc-alkaline volcanism related to extensional tectonic activity is widespread in Western Anatolia. Simav Graben is the latest product of this tectonic regime and includes a wide range of ore deposits and hydrothermal mineralizations.

One hundred samples collected from the surface and cores in the alteration zones of Simav Graben were investigated by XRD, SEM and FTIR. Two types of hydrothermal alteration zones were identified: 1) hydrothermal alteration related to quartz porphyry intrusions and 2) hydrothermal alteration related to epithermal quartz veins. Close to the quartz porphyry intrusion the dominant clay mineral is mixed layer illite/smectite while at a distance of about 20 m dickite is dominant and the mixed layer clay minerals are absent. Secondary quartz and alunite are the non-clay minerals in each zone. The clay mineral sequence from inner to the outer parts of the quartz veins is as follows: kaolinite + illite→ mixed layer illite/smectite + kaolinite→ smectite. Quartz and feldspars of volcanic origin accompany the clay mineral paragenesis.

The presence of quartz-dickite indicates the formation temperature of about 160-200°C, while the transformation of illite/smectite to illite occurs at ~230°C [1,2]. The assemblage kaolinite + illite indicates a temperature of around 200-250°C. It is therefore concluded that the temperature of the hydrothermal fluids was ~200°C in the region.

Hydrothermal alteration is controlled by a fault system, which allows intrusion of quartz porphyry dikes and quartz veins. The presence of alunite and dickite is indicative of an acidic sulfate alteration [3]. On the other hand, alteration around the quartz veins indicates acid to intermediate type of alteration [1].

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Mysterious silver microparticles of the Cretaceous-Paleogene boundary Fish Clay (Stevns Klint, Denmark)

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Instrumental neutron activation analysis (INAA) showed the Ag concentration in the Fish Clay is about 1.0 ppm and that its carbonate-free fraction contains about 2 ppm. Alvarez et al. [1] determined the Ag concentrations in the whole Fish Clay (1.2 ppm) and in its carbonate-free fraction (3.5 ppm). In order to evaluate the overall (terrestrial or extraterrestrial) source of Ag in the smectite of the Fish Clay, we compared these data with Ag contents in normal seawater, sediments, soils, igneous rocks (basalts having the highest content), upper continental crust, mantle and chondrites (Table 1). The Ag content of the Fish Clay is much higher than in seawater, sediments, soils, igneous (basaltic) rocks, crust or mantle. Thus, it is likely that none of these sources were capable to supply Ag to the Fish Clay. The concentration of Ag in the Fish Clay is approximately twenty times higher than its average content of chondrites. Consequently, it is likely that most of Ag in the Fish Clay is of the terrestrial origin.

Table 1: Ag content of the Fish Clay and potential suppliers of Ag

Rock	Ag [ppb]
Fish Clay	2×10^{3} (this work)
Seawater	2×10^{-3}
Sediments	120
Soils	700
Igneous (basaltic) rocks	37-110
Upper continental crust	530
Mantle	2.92-19
Chondrites	97-107

We also report here a new find of the occurrence of micrometer-sized silver (Ag) particles in the red layer of the Fish Clay that appear to have been embedded into the biogenic calcite matrix. 100 of these microparticles (AgMPs) were hand-picked under a binocular stereomicroscope. Energy dispersive X-ray analysis (EDS) analysis (Fig. 1A) indicates that these microparticles are composed of pure silver (>99 % of the total weight).

Stereomicroscopy shows that the AgMPs are shiny black or light brown. SEM images show that their shapes are irregular and predominantly rounded with rugged surfaces that often contain a few pits and voids (Fig. 1B). Aggregates of numerous AgMPs are spherical (Fig. 1C), and some of them exhibit dendritic textures (Fig. 1D).

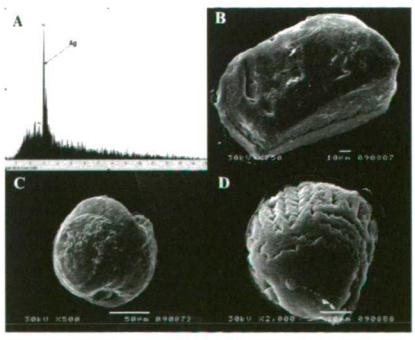

Fig. 1: Ag microparticles from the red layer of the Fish Clay: (A) EDS spectrum; and SEM micrographs of samples: (B) rounded; (C) common spherical; (D) spherical with dendritic surface texture.

[1] Alvarez, L.W. et al. (1980) *Science*, **208**, 1095-1108.

Geochemistry of the Cretaceous-Paleogene boundary (Fish Clay) at Stevns Klint, Denmark: Au in the basal black marl

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The Fish Clay (of earliest Danian age) at Højerup belongs to one of the classic Cretaceous-Paleogene boundary deposits at Stevns Klint. This boundary clay constitutes four distinctive layers: the latest Maastrichtian bryozoans-rich chalk, a 2-5 cm thick basal black marl, brown-to-grey marl and grey marl overlain by the lower Danian Cerithium limestone Member. Black and brown-to-grey marls represent the main part of the Fish Clay. The mineralogy of the black marl is comparatively simple, smectite and authigenic (mainly biogenic) calcite being the principal components.

We report here the study of Au in the black marl and in its inorganic (carbonate, smectite, silicate) and kerogen fractions. The selective leaching procedures were used to establish geochemical associations and specific mineralogical residences for Au. The sample was analyzed by instrumental neutron activation analysis (INAA).

Table 1: Geochemical data for Au of basal black marl

Metal		Fraction*				
		Total	Carbonate	Smectite	Silicate	Kerogen
Geochemical concentration						
Au	[ppb]	25	0	35	10	475
Geochemical distribution						
Au	[ppb]	25	0	15	<5	10
	%	100	0	60	6	34

*The percentage of the whole sample: carbonate [52.0 %], smectite [21 %], silicate [25.2 %], kerogen [1.8 %]

The analytical results (Table 1) indicate that most of Au resides in the smectite (60 %) and kerogen (34 %). We suggest that a substantial amount of this metal was probably contained in the detrital smectite (and kerogen) arriving at the site of deposition. Preliminary considerations implied that Au in the black marl could have been both of terrestrial and of meteoritic origin.

Cation exchange capacity (CEC) – a tool for determination of secondary alteration of chlorite from Fore Sudetic Monocline (western Poland)

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Chlorites are very common metamorphic and hydrothermal minerals composed of Mg, Fe, Al and Si. They are phases, which can be unstable during retrogressive metamorphism or late stage hydrothermal alteration.

Chlorites from Bolewice-1 borehole (western Poland) were studied using XRD and EMPA methods. Diffraction data indicate that the chlorites are usually altered. The aim of this study was to find a tool suitable for the analysis of spatial differences in the degree of alteration. CEC was applied to determine changes in degree of chlorite alteration in thin section scale. There procedure proposed by [1] using in situ Cs saturation on thin sections and electron microprobe analysis was applied.

There are two factors controlling CEC of partly altered chlorites. First of them is late fluid migration producing vermiculitization of chlorite and the second one is K-metasomatism and celadonite formation which can close the crystal structure to Cs.

The main factor controlling chlorite alteration under retrograde conditions is the contact with migrating fluid. EMPA data collected from samples saturated with Cs indicate that there is strong decrease in CEC in the case of amygdules with good sealing, where secondary fluids couldn't migrate. In these cases CEC can have values less than 3 meq/100 g even if there was no K-metasomatism, whereas clays, which fill pseudomorphs after pyroxene indicate highly differentiated values, usually from 8 to 11 meq/100 g, sometimes even higher than 12 meq/100 g. These values are lower than reported before for mixed layer phases [1], but evidently higher than values proposed for pure chlorite, which should not have any CEC. Moreover, CEC varies between samples from different depths and sometimes indicate values in range 4 – 6 meq/100 g. This is in agreement with XRD data showing different degrees of chlorite alteration.

Celadonitization affected both clays from the amygdules and pseudomorphs and was probably a relatively early process, forming celadonite layers in amygdule fillings. It is connected with the decrease of CEC to values smaller than 5 meq/100 g because K stabilizes crystal structure and does not allow for Cs incorporation into it.

Results of this study indicate that CEC is extremely useful for some type of investigations in clay mineralogy. It allows for discrimination of spatial changes in clay mineral distribution connected with their partial decomposition and alteration, giving us insight into late fluid migration development during hydrothermal metamorphism.

[1] Schiffman, P. & Southard, R.J. (1996) *Clay. Clay Miner.*, **44(5)**; 624-634

Bentonite; its resources and geological settings in Iran

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Bentonite is a swelling clay rock known to Iranians for ages. Old famous scientists like Avicenna and Ebne Bitare mentioned this material, which was named clay soap (1173), taylorite (1888) and bentonite (1897). Its name is derived from the shaly Benton Formation in the U.S.A. Smectite minerals are the main components of bentonite.

Bentonite often forms in warm and humid environments such as lagoons and shallow coastal areas, which are oxidation zones with basic pH of 8-9. The source rocks of bentonites are acid volcanic rocks ranging from dacite to rhyolite. When these volcanics enter into aforementioned environments they undergo bentonitization process, which may be followed by the burial diagenesis alteration.

So far more than 70 bentonite deposits have been identified in Iran. Most of these deposits formed in the Eocene and Oligocene, i.e. during the time period with intense acid volcanic activities. No bentonite deposit has yet been found in the vicinity of plutonic bodies in Iran. In most cases, the bentonite deposits occur along the contact with acid volcanic rocks. Comparing the distribution map of bentonite deposits with the geological map of Iran, one finds the genetic relationship between these deposits and the volcanic rocks.

The age of the world's bentonite deposits ranges from Jurassic to Pleistocene. There are large reserves of the Cretaceous bentonite in the U.S.A., Europe and Asia. But most of the world's bentonite deposits belong to the Tertiary.

All bentonite deposits in Iran formed after Cretaceous. The absence of large-scale acid volcanism and presence of an exceptional marine environment dominating Iran during the Cretaceous period could explain the formation of bentonite deposits in Iran after Cretaceous. Near 40% of bentonite deposits of Iran formed in the Eocene, and there is almost equal number of the deposits of the Oligocene-Miocene age.

Lower Paleozoic K-bentonites and their application for tectono-stratigraphic correlation in Europe and North America

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Continuing studies of Ordovician and Silurian K-bentonites in Europe and North America show that many of them are distributed regionally and thus can serve as important marker horizons for stratigraphic correlation. Two examples of projects underway are from the Carnic Alps in Austria and the North American midcontinent. Lower Paleozoic K-bentonites occur in a region of the Carnic Alps that is characterized by a metamorphic overprint ranging from anchizone to epizone. As a consequence of this thermal history, the illite/smectite clay mineralogy that commonly characterizes such beds has been altered to illite and chlorite, similar to the clay minerals found in associated mudrocks. The volcanogenic origin of these beds is confirmed, however, by the presence of primary magmatic phenocrysts of biotite, apatite and zircon. In some samples the zircons show evidence of magmatic resorption. Four horizons fall approximately within the *amorphognathoides* zone at the Oberbuchach section and eight in the Lower Wenlock, which appear to be traceable across the Cellon, Oberbuchach and Nölbling sections. The K-bentonite sampled from the Uggwa section may be of a similar age to those from the Llandovery of Nölbling Graben. Sixteen levels have been recorded from the *vesiculosus* zone and upwards within the Rhuddanian and eleven from the *triangulatus* zone (Aeronian). The abundant presence of these horizons in the Llandovery sequences of the Carnic Alps is similar to those in the British Isles, Sweden, Canada and North America and documents widespread volcanism related to the closing of the Iapetus Ocean and northward drifting of microplates derived from the northern margin of Gondwana. The Osmundsberg K-Bentonite has been recognized throughout NW Europe in the late Llandovery (Telychian) and it is probable that this level may also be identified from the samples taken at this stratigraphic level from the Cellon, Seewarte and Oberbuchach sections (*celloni* zone).

Although Gondwana was tectonically quiescent during the Silurian, Laurentia experienced at least two separate phases of collision. Evidence can be found in the basal Silurian strata of the Appalachian Basin in the form of widespread sheet sands and shale successions, K-bentonites, and zones of soft-sediment deformation. K-bentonites have been positively identified at multiple levels in the Llandovery-Wenlock interval in eastern North America.

For the Silurian rocks of the Cincinnati Arch in Ohio, Kentucky, and Indiana seven depositional sequences are assigned on the basis of through-going unconformities that mirror those already recognized in the early Llandovery to early Ludlow of the northern Appalachian Basin. Revision of the conodont biostratigraphy for the Cincinnati Arch by previous authors has produced results that both agree and disagree with the other lines of data implemented in the sequence stratigraphic depositional model. Biostratigraphic correlations between southern Ohio and the Niagara Falls area are largely in agreement with correlations based on other lines of data, such as K-bentonite evidence, as are correlations between west-central and western Ohio, southeastern Indiana, and northern Kentucky. The integrated analysis suggests a relatively simple history of high-frequency relative sea level fluctuations superimposed on a tectonic signature of long-term basin subsidence and very slow forebulge migration.

Comparative investigation of Sarmatian bentonites in the region of Miskolc (North Hungary)

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During the complex mapping and investigation of the north-eastern foreland of the Bükk Mountains, our research team noticed an extensive Sarmatian (Upper Miocene) volcanic-sediment series. The Lower and Upper Sarmatian succession showing similar lithological characteristics is subdivided by a widespread extraclastic andesite tuff. The incomplete, eroded sections of these formations occur in numerous locations in the region of Miskolc and Putnok. The thickest and most uniform sediment series is located in Sajóbábony, 5 km to the north of the city of Miskolc. This area was explored at the turn of the millenium with the support of the Széchenyi Program [1,2].

The age of the Sarmatian series was determined on the basis of bivalve fauna and by K/Ar radiometric analyses. Complex analyses were carried out on the material of the bentonitic sequence, including major and trace element analyses and several hundred X-ray diffraction and thermal analyses in order to give a horizontal and vertical, qualitative and quantitative characterisation of the bentonite deposit [3].

Another significant bentonitic sequence is located in the Avas Hill, in the city centre of Miskolc. The underlying extraclastic andesite tuff of the Sajóbábony bentonitic sediment series appears to be the overlying bed of the Avas Hill. The Sarmatian sediment sequence is found under the andesite tuff with a vertical extent of about 80 m. This sequence is composed of alternating bentonite and sandstone layers. On the basis of observations and geodetical measurements of more than a hundred outcrops, the thickness of the bentonite layers varies between 0.5 – 3 m, despite the frequent alternation of layers of different lithology. The characteristics of the bentonite layers in the Avas Hill are very similar to the sediment sequence of the Sajóbábony bentonite deposit. Weathering products of acid tuff in shallow-sea environment were identified in both locations. Both bentonitic sediment deposits contain 30 – 70 % poorly crystalline montmorillonite.

The aim of this presentation is to give a comparative mineralogical and geochemical insight regarding the two sediment sequences, and is to give an overview on the Sarmatian sequence and the processes of the shallow-marine environment from an economic geological and paleoenvironmental point of view.

[1] Kozák, M. & Püspöki, Z. (2003) *Summary final report of the geological exploration of the open air permitted bentonite research called 'Sajóbábony-Sajókeresztúr'*. Archive of Dept. of Mineralogy and Geology, University of Debrecen, Archive of Hungarian the Geological Service, Salgótarján (in Hungarian) [2] Püspöki, Z. et al. (2008) *Clay. Clay Miner.*, **56(1)**, 23-38. [3] Püspöki, Z. et al. (2003) *Földtani Közlöny*, **133(2)**, 191-209 (in Hungarian).

Hydrothermal kaolinite occurrences of the Gediz area (Kütahya, western Anatolia, Turkey)

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The kaolinite occurrences at Akçaalan and Sazak (Gediz area, Kütahya, western Anatolia) formed by hydrothermal alteration of the Civanadağ tuffs and Akdağ volcanites in relation to Miocene volcanism, resulting in the development of a silica cap and iron-oxide/-oxyhydroxide veins, with local precipitation of pyrite. These units were studied via petrography, reflected-light polished-section microscopy, X-ray diffractometry, differential thermal analysis-thermal gravimetry (DTA-TG), scanning electron microscopy (SEM-EDX) and geochemical methods. Petrographically, the volcanites comprise andesite, rhyolite and tuff. Plagioclase and K-feldspar are argillized, biotite and hornblende are opacitized, groundmass is argillized, and Fe-oxide/-hydroxides are widespread in these volcanic units. Mineralogical zonation, such as kaolinite+opal-CT in the inner zone and smectite+illite outward, is observed. Kaolinite, quartz, smectite, illite, opal-CT, feldspar, calcite and dolomite were all determined in these rocks. Micromorphologically, kaolinite is well-crystallized and of vermiform character. SiO_2 of the bulk rocks vary from 52.06 to 70.91%, and Al_2O_3 from 14.71 to 20.77%. Despite increasing SiO_2, Al_2O_3 and Fe_2O_3+TiO_2 decrease laterally, and Fe_2O_3 increases upward. Decreasing Sr values suggest degradation of feldspar at low temperatures. Albitization is compatible with decreasing Rb and K contents. Al was enriched during hydrothermal alteration, in contrast to other elements, which were depleted. All samples are enriched in large-ion lithophile elements (LILE) and light rare-earth elements (LREE), and depleted in high-field-strength elements (HFSE) and heavy rare-earth elements (HREE) with respect to primitive mantle and chondrite. Negative Eu anomalies, relative to chondrite, reflect alteration of feldspar. Field observations along with mineralogical and geochemical determinations reveal that kaolinites of the Gediz area developed by hydrothermal alteration of feldspar, hornblende and volcanic glass within the volcanites.

Mineralogy and environment of the Qarain clay deposits, Riyadh region, Saudi Arabia

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The Qarain area is about 220 km west of Riyadh city, capital of Saudi Arabia. The Qarain clay deposits lie within the Marrat Formation (Lower Jurassic). They are characterized by the dominance of kaolinite clay mineral. Illite occurs in a lesser amount in the clay fraction. The dominant non-clay mineral is quartz. X ray diffraction analyses were obtained using Ni-filtered K_α radiation from a Philips (PW1050).

It is suggested that the clay deposits were the result of partial laterization of the source rocks, mainly acid igneous rocks of the Arabian shield. Partial laterization occurred under humid tropical conditions. The weathered rocks were transported to the present area and deposited in a shallow and near shore environment of the Toarcian Sea.

The concentration of boron in the 20-2 micron grain size fraction is higher than 50 ppm with an average value of 73 ppm, while the average value of boron is 41 ppm in the finest fraction of 2 micron. It is suggested that the high B contents in the 20-2 micron size fraction largely derived from the source rocks, may indicate a non-marine origin for the Qarain clay deposits.

Stable isotopes in clay minerals from the Northern Alpine Molasse basin as archives for alpine climate and elevation change

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The stable isotope composition of oxygen and hydrogen in rain water correlates with the air temperature and with the altitude of precipitation. If meteoric water is taken up into the structure of minerals with a known water-mineral fractionation factor, it is possible to reconstruct its original $\delta^{18}O$ and δD values from the isotopic composition of the host mineral.

Our study aims on reconstructing the oxygen and hydrogen isotopic composition of Miocene water via the analyses of clay minerals from different origins across the European Alps and the north Alpine foreland basin, the so-called Molasse basin. As clay minerals are hydrous, they contain both hydrogen as well as oxygen, allowing the use of both isotope systems to reconstruct the paleoprecipitation. Measurements were carried out on clay mineral separates from Molasse sediments from the northern foreland, covering the deposits from western Switzerland, via southern Germany, the Vienna Basin to the Pannonian Basin, with a sedimentation age from 8.5 to 19.2 Ma. Fossils from the same samples (ostracods, foraminifera, shark teeth, mammal remains) have already been analysed in previous studies for their O and Sr isotope composition [1, 2]. It is the aim of this study to compare the results from both the marine as well as the detrital record in order to address climatic as well as elevation changes in the Alpine region during orogenesis.

Prior to analyses, the material was treated with HCl to remove carbonates and separated to grain size fractions of <2μm, <0.5μm, and <0.2μm by centrifugation based on Stokes' law. XRD measurements were made to determine the mineralogical composition. Smectite and mixed layer minerals, determined with glycol treatment, dominate the clay fractions. SEM analyses of the clays support a detrital origin.

Oxygen isotopes were measured using CO_2 laser fluorination and hydrogen isotopes using high temperature reduction (TC/EA) on dried separates. The values of the <2μm fraction have a range of 14.1‰ to 21.2‰ for $\delta^{18}O$ and –143 to –102 for δD, relative to VSMOW. For hydrogen, a clear grain size dependence was observed, smaller particles have lower δD values down to –164‰, with a non-linear trend. The $\delta^{18}O$ values have no clear relation with grain size. It also appears that there is no overall correlation between the δD and $\delta^{18}O$ values, which indicates that both tectonic and climatic variations may have influenced their isotopic compositions.

An application of the relations proposed by [3] to calculate the $\delta^{18}O$ values of water in equilibrium with the clays and the temperature of clay formation suggests $\delta^{18}O$ values that may be as low as –8 to –9 for the water in the <2μm fraction and temperatures of 10-20°C, both of which are typical for modern precipitation in the circum-alpine region today.

Ongoing research will include sampling more material from the Molasse basin for a better spatial and temporal coverage.

[1] Janz, H. & Vennemann, T. (2005) *Palaeogeogr. Palaeocl.*, **225**, 216-247. [2] Kocsis, L. et al. (2007) *Geology*, **35**, 451-454. [3] Delgado, A & Reyes, D. (1996) *Geochim. Cosmochim. Ac.*, **60**, 4285-4289.

The distribution of late diagenetic illite and kaolinite in Rotliegend aeolian sandstones from the Fore-Sudetic Monocline, SW Poland

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In terms of hydrocarbon prospecting, Rotliegend aeolian dune sandstones from the Fore-Sudetic Monocline constitute a good target. Their reservoir properties depend primarily on diagenetic clay minerals, which not only are the most abundant among authigenic phases but also dominate the grain surface area. Whereas illite is by far the most ubiquitous diagenetic phase, other clay minerals occur locally. The mutual relationship between late diagenetic illite and kaolinite was studied for the south-eastern part of the Fore-Sudetic Monocline, where these two minerals are common, by a combination of methods (polarising microscopy, XRD, SEM, XRF).

The Rotliegend sandstones are buried at a depth of ca. 2000 m in the area studied, which is the minimal burial after a two-stage Mesozoic inversion. Three distinct sandstone types were observed: (a) kaolinite-rich arenites devoid of detrital feldspars, (b) illite-rich arenites with scarce detrital feldspars, and (c) feldspar-bearing arenites (av. 10 vol% Fsp) containing fibrous illite. Individual types occur in adjacent wells, distant from several hundred meters to 1-2 kilometres. The illite and kaolinite exhibit features of late diagenetic minerals that crystallized after significant compaction and post-dated other diagenetic phases (hematite, dolomite, quartz). The fibrous illite co-occurs with the kaolinite in some wells. Also, the remnants of kaolinite dissolved flakes with illite growing on them were observed under SEM.

A relatively small area studied and one sedimentary facies (aeolian dune) allow assuming similar initial parameters, such as framework grain composition and porosity. Therefore, the crystallization of late diagenetic kaolinite (a) and illite (b) must have been associated with a pore-fluid flow and the alteration of detrital feldspars whereas the fibrous illite (c) crystallized independently at a later stage without feldspar dissolution. A model proposed by Gaupp et al. [1] of acid pore-fluids originated from Carboniferous coal-bearing rocks juxtaposed Permian sandstones along faults is in accord with the case studied. The pore-fluid flow resulted in kaolinite crystallization in the vicinity of faults and illite formation in more distant zones from more neutralized fluids.

[1] Gaupp, R. et al. (1993) *AAPG Bull.*, 77, 1111-1128.

K-Ar ages versus grain size and illite Kübler index: a case study of parametamorphic rocks from eastern Mt. Papuk, Croatia

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One of the frequent and most important problems in K-Ar dating is the contamination with detrital materials which can results in hard to interpret mixed ages. The coarse fraction isolated from samples is most often heterogeneous i.e. composed partially of detrital minerals and of more recent authigenic minerals which grew as a result of post-depositional thermal processes. Variable age mostly depends on the proportions of detrital and authigenic phases, both of which are considered to have a fixed K-Ar age. On the contrary, it is generally assumed that small grain-size fractions (e.g. <2 μm fraction) are mostly devoid of the detrital mica, while their K-Ar age represents the "mix age" of different generations of illitic minerals present within it.

A special attention here was paid to the evaluation of the influence of detrital minerals by observation of variation in K-Ar ages and illite Kübler index (KI) obtained on different grain-size fractions. Samples of high temperature anchizonal to epizonal altered parametamorphic rocks, representing various lithologies with different petrographic characteristics and stratigraphic age were used for this purpose.

Some trends can be observed. The decrease of K-Ar ages with decreasing grain-size (Fig. 1) can be attributed to an increase of diffusion of radiogenic ^{40}Ar resulting in increasing reset of the K-Ar system with decreasing grain size and to a reduction of detrital minerals contamination effect which becomes less and less pronounced as grain size decreases. Furthermore, KI of the finer fractions increases with decreasing grain size showing negative correlation with decreasing K-Ar ages. This effect is closely connected with the prolonged formation of illitic minerals and their wide temperature stability.

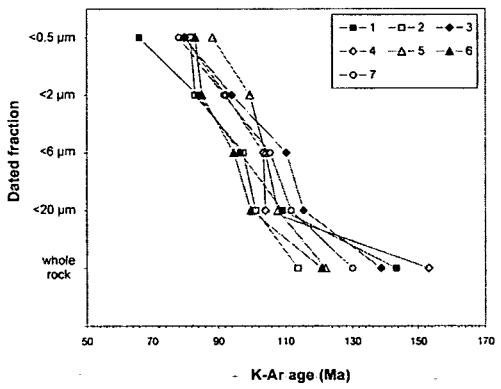

Fig. 1: K-Ar ages determined for different grain size fraction of analysed samples (1- chlorite schist; 2 - chloritoid schist; 3 - metasandstone; 4 - quartzite; 5 - phyllite; 6 - phyllitic metaconglomerate; 7 - quartz metasandstone).

Clay mineralogic evidences for a Mid Paleozoic tectono-thermal event in Zonguldak Terrane, NW Turkey

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The Zonguldak Terrane (ZT), a Gondwana-derived continental microplate [1] along the Black Sea coast in NW Anatolia, was believed to comprise more or less continuous Paleozoic successions. It was considered to be rifted off the northwestern Gondwana-margin in the Early Paleozoic and drifted across the Rheic Ocean during the Mid Paleozoic and successively accreted to Laurasia along the Eastern European Suture during the Variscan Orogeny [2]. Along several cross-sections in ZT, the siliciclastic rocks of Ordovician to Middle Silurian age overlay unconformably a Cadomian basement with orthogneisses, oceanic and island-arc sequences. Late Lower Devonian quartzites unconformably overlay Middle Silurian (Wenlock) graptolitic shales, indicating an important event.

This study aims to investigate whether this unconformity is accompanied by a thermal event, and hence to trace the fingerprints of an orogenic overprint. For this, the diagenetic characteristics of the Paleozoic sedimentary rocks in ZT are investigated by means of petrographic and X-ray diffraction methods. Clay mineralogic associations, Kübler Index value (KI), *b* cell dimension (Å) and polytype of illites are determined throughout Ordovician-Carboniferous units. Siliciclastic and calcareous rocks mainly contain phyllosilicates, quartz, feldspar, calcite, dolomite, hematite and goethite minerals. Phyllosilicates are represented by illite, chlorite, kaolinite, mixed-layered chlorite-vermiculite (C-V), chlorite-smectite (C-S) and illite-chlorite (I-C). Quartz and clay/phyllosilicate minerals are common in all formations, whereas the amounts of feldspar, calcite and dolomite increase in some levels. The main phyllosilicate assemblages of Ordovician-Silurian units are illite + chlorite + I-C ± C-V ± C-S, whereas Devonian-Carboniferous units have illite + kaolinite + chlorite. The appearance of kaolinite and the absence of chloritic mixed-layers in the Devonian units is the main difference in terms of the clay mineral association. KI values of Ordovician-Silurian and Devonian-Carboniferous units (0.58 ± 0.18 and 1.13 ± 0.24 $\Delta°2\theta$) reflect late diagenetic and early diagenetic grades, respectively, and show sudden jump from Silurian to Devonian. The *b* cell dimension values of illites of Ordovician-Silurian units (9.011 ± 0.013 Å) are somewhat higher than those of Devonian-Carboniferous units (8.998 ± 0.012 Å). Illites are composed of a mixture of the $2M_1$, $1M$ and $1M_d$ polytypes. Ordovician-Silurian units have $2M_1$ and $1M_d$, whereas Devonian-Carboniferous units include $1M$ polytype in addition to $2M_1$ and $1M_d$ polytypes.

In brief, the new mineralogic data indicate that the pre-Middle Devonian rocks in ZT experienced a tectono-thermal event, prior to the Middle Devonian transgression. This Caledonian-time event is also reported in some Balkan-Moesian terranes but not noticed in the neighboring Istanbul Terrane, supporting a complex terrane distribution [3] at the S margin of Laurasia, prior to the Variscan closure of the Rheic Ocean.

[1] Goncuoglu, M.C. (1997) *Turkish Assoc. Petrol. Spec. Publ.*, **3**, 13-23. [2] Goncuoglu, M.C. (2001) *ESF Europrobe Meeting*, Ankara, 22-23. [3] Yanev, S. et al. (2006) in Robertson, A.H.F. & Mountrakis, H.F. (eds.) *Tectonic Development of the Eastern Mediterranean Region*. Geol. Soc. London, **260**, 51-67.

Clay minerals composition: a significant tool for glacial till studies and paleo reconstruction, with a reference to the glacial history in Drenthe - the Netherlands, North West Germany and the Baltic

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Till deposits reflect glacial history of landscapes. That is the main reason to have good knowledge about tills for paleo-reconstruction of glaciations and a better understanding of the impact of glacial processes on actual eco(-hydro)logical relationships. For sustainable protection and development of nature- and landscape-values more insights in till deposits are therefore necessary. That is the main conclusion of a recent study in Drenthe, the Netherlands [1].

The aim of our study is to verify a new glacial model. To differentiate glacial tills and sedimentation conditions for (i) glaciations (Saale, Weichsel) in the Netherlands, Germany and the Baltic; (ii) stages within glaciations in Drenthe and (iii) supposed phases within one stage with attention to local conditions.

XRD analyses of clay minerals confirm conclusions of formerly used analyzing techniques (e.g. shear stress-measurements). Clay minerals and their structures are tools to differentiate tills from different stages and phases of surging at a lower level. Contrary to other methods quarries are not needed for sampling. So the method opens more possibilities for sampling and studying tills at more places in areas with a lack of quarries like in Drenthe province.

Our study shows that clay mineral composition in glacigenic sediments indicates significant influence of glacial sedimentation conditions such as sediment transport and postsedimentation changes. Vermiculite is a clay mineral that indicates postsedimentation changes – weathering and soil forming processes. Various mineral compositions may indicate sediment mixing due to surging processes. It was possible to separate different till forming stages.

Our final conclusion is that clay minerals are a useful tool for paleo environmental reconstruction of glacial landscapes of different ages, which give more information about positional, local conditions of formed tills. We showed that in Drenthe, the Netherlands, tills are formed under saltwater conditions whereat indicate authigenic minerals (basanite, halite, syngenite) in fraction < 0.2 μm. The influence of pro- and subglacial processes to surface pressed up deep groundwater changed till composition and weathering products does have also an ecological impact.

[1] Bregman, E.P.H. (2007) *Ph-D research plan.* Internal document.

TEM-AEM study of hydrothermal smectite formation in Fe-Mn-metalliferous sediments: samples from the HMS Challenger expedition (1872-1876)

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The aim of this study is to investigate the formation of smectite in three samples of submarine Fe-Mn-metalliferous sediments of hydrothermal origin, collected by the British HMS Challenger during the first oceanographic expedition (1872-1876). They were collected from the seafloor in the vicinity of the Pacific-Antarctic Ridge and the Chile Ridge. Firstly, the samples were analyzed by means of XRD, chemical analysis, SEM-EDX and IR. After removal of biogenic calcite, the results from the above techniques indicated that they consist mainly of two amorphous or semiamorphous phases intimately mixed: Fe-Mn oxyhydroxides and a Si-Al-Mg-Fe phase of chemical characteristics similar to smectite and with variable proportions of the above elements.

The TEM-AEM study was carried out to complete the previous data. The analysis, obtained from powders dispersed on holey C-coated formvar Au grids, showed the morphological and chemical characteristics of the several components of the sediment. To clearly identify mineral phases, SAED patterns, High-Resolution images and microanalyses were correlated. The appearance of Fe-rich oxyhydroxides, as round-shape particles, is clearly different from that of the other phases. Mn-rich oxides, previously identified by XRD as the δ-MnO_2 phase, related to birnessite, aggregate to form high-contrast clusters with an apparently layered structure. Smectite particles have the typical flaky and wavy morphology of smectite with the particular presence of relative large basal plates. These smectite particles always appear associated to Fe-Mn oxyhydroxides. Smectite composition corresponds in most cases to nontronite, frequently containing a trioctahedral (Mg-rich) component, although there are compositions corresponding to Fe-montmorillonite and Al-montmorillonite. No Mn-rich smectite was detected but Mn abundance is significantly greater than in typical smectites of other geological environments. Electron diffraction patterns confirm the poor crystallinity of both Fe-Mn oxyhydroxides and most smectite particles. These results are interpreted as representing hydrothermal smectite formation from Fe-Mn-rich metalliferous sediments as the Fe-rich gels react with solid particles and dissolved species. Possible sources of Si, Al and Mg are detrital silicate minerals, glass of basaltic origin, silica gel precipitated from hydrothermal fluids and seawater as the main source of Mg.

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Climate recorded by clay minerals from surface sediments of Lake Kusai, the Hoh xil Area, China

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Lake Kusai is selected as research area because it is located in natural safeguard area of the Hoh xil, northern Tibetan Plateau, having too bad natural environment and only weakly influenced by human activity. Present work is aimed at studying the relationship between clay minerals in surface sediments of a lake from high cold region and its climate in recent years.

23 surface sediment samples and their corresponding three oriented aggregates (natural air-dried, glycolated, and heat-treated) of clay minerals were studied by X-ray powder diffraction. The bulk rock results show that major detrital minerals are quartz, feldspar, and calcite, the content of summation is 65%-80%; minor phases are aragonite, gypsum, dolomite, and amphibole. The clay mineral content of the bulk rock samples is 15%-33%. Based on the analysis of oriented specimens, and according to the distribution of illite/smectite mixed-layer (I/S), we plot four districts (Fig. 1).

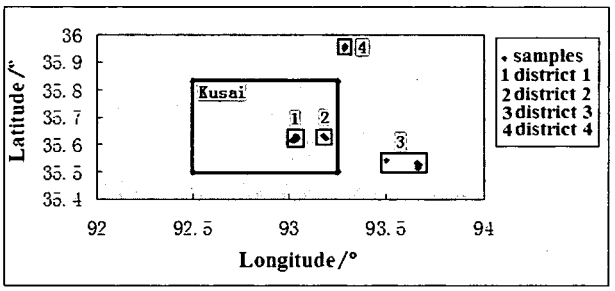

Fig. 1: Samples distributions in Lake Kusai and its nearby.

Clay minerals mainly comprise of illite (65%-82%), chlorite (12%-23%) and kaolinite (5%-7%). 4-15% ordered I/S mixed-layer appears in district 1 and 3 rather than district 2 and 4 (Table 1). Illite and chlorite as major clay minerals indicate that the whole lake area has been dominated by arid and cold climate conditions in recent years. I/S mixed-layer appearing at local areas may indicate the climate had ever undergone alternately arid-humid environment within a short period of time.

Table 1: Qualitative and semi-quantitative clay mineralogical composition, CI and IC values of illite of studied samples

Distribution	Illite	Chlorite	Kaolinite	I/S	CI	ICr	ICa
district 1	66-78%	12-24%	5-7%	5-15%	0.21-0.33	0.41-0.58	0.51
district 2	65-82%	12-25%	5-6%	0	0.27-0.35	0.30-0.46	0.39
district 3	65-77%	12-21%	5-6%	4-12%	0.24-0.33	0.43-0.58	0.48
district 4	70-74%	20-23%	5-6%	0	0.32-0.36	0.34-0.39	0.37

CI-Chemical Index of illite, ICr- IC value range, ICa –IC average value

Five international standard illite samples (provided by Prof. L.N.Warr, Germany) were tested to correct for the experimental conditions, making the data directly comparable to the international standards. The corrected illite crystallinity values (IC) of the samples from district 1and 3 are higher than those from district 2 and 4. Chemical Index (CI) values of illite are less than 0.5 indicating that it is the result of physical weathering, and possesses of Fe-Mg. Therefore, we assume that a weak hydrolysis occurs in our research area, and its intensity in district 1 and 3 is stronger than in district 2 and 4.

In conclusion, we have obtained initial results between clay minerals and the climate, and the formation mechanism of clay minerals in Lake Kusai will be studied later in details.

On spatial-temporal variations of secondary phases formed during mud diagenesis

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Chemical compaction of soft muds to shales during burial leads to large changes in rock-physical properties like stiffness porosity and permeability. The smectite to illite dissolution presippitation reaction releases surplus silica that is precipitated as fine-grained (1-3μm) pore-filling quartz crystals [1-3]. Surplus magnesium and iron is precipitated in chlorites, or if calcium carbonate is present may be precipitated as ferroan dolomites.

In this study the spatial distribution of secondary phases by varying the effective diffusion coefficient and initial spatial distribution of mineral phases have been explored using the PHAST 3D-reactive transport code. The initial system consisted of a 1 mm cube divided into smectite-rich and smectite-poor domains discretized into 720 cells.

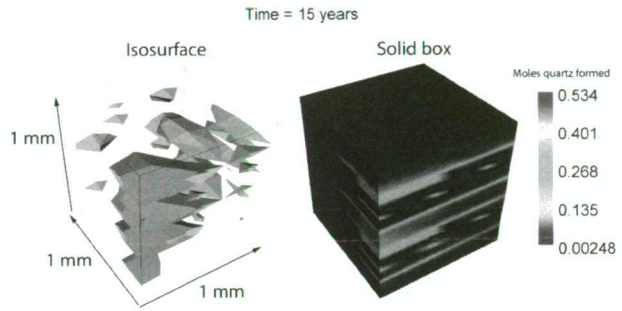

Fig. 1: Spatial distribution of quartz formed at 80°C. Local quartz formation is dominated in the gradients between the smectite-rich low-diffusivity domains and local K-feldspar. The blue colors denote low/no formation of quartz in smectite-rich domains.

Preliminary simulations suggest that quartz and illite formation is dominated in chemical gradients forming locally between K-feldspar and smectite. As magnesium builds up the transformation slows down and may be locally constrained by the precipitation of the magnesium and iron sink (chlorite or ferroan dolomite, in addition some iron and magnesium is incorporated into illite). Low effective diffusion rates leads to strongly localized illite and quartz precipitation, whereas increasing the effective diffusion coefficient results in more dispersed precipitation. Strongly localized microquartz formation observed in cemented mudstones [1-3] support that low diffusivity and the initial spatial distribution of mineral phases controls the spatial distibution of the secondary phases.

[1] Thyberg, B. et al. (2009) *First Break*, **27**, 27-33. [2] Thyberg, B. et al. (2009) *Mar. Petrol. Geol.* (in press) Doi:10.1016/j.marpetgeo.2009.07.005. [3] Thyberg, B. & Jahren, J. (2010) *AAPG Bull.* (submitted).

Chemical weathering intensity and clay minerals in Plio-Pleistocene red clays (Hungary)

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The Tertiary red clays in the Carpathian Basin of Hungary (Tengelic Red Clay Formation: TRCF; Kerecsend Red Clay Formation: KRCF) are overlain by loess paleosol sequences named Paks Loess Formation (PLF) in S Transdanubia. The thickness of the red clay ranges from 4 to 90 m. The red clay sediments are known from both exposures and boreholes. The age of these formations is ~3.5–1.0 Ma.

Elemental oxide analyses of the red clays were performed by X-ray fluorescence (XRF), and the X-ray powder diffraction (XRD) was used for mineral identification. In this study, we aim to determine the changes of clay minerals due to chemical weathering and age.

As shown in the A–CN–K diagram (Fig. 1), the samples are distributed along the joint A–CN and tend to approach the A-pole, reflecting a process in which K_2O, CaO, and Na_2O are leached out and Al_2O_3 is enriched in the samples, i.e. mineralogically, the dissolution of feldspar minerals and the production of clay minerals (smectite, illite, and kaolinite).

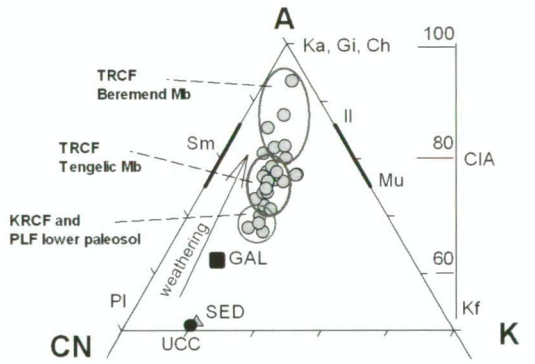

Fig. 1: Basic A–CN–K (Al_2O_3–CaO + Na_2O–K_2O) ternary diagram with CIA values showing the weathering trend of red clays. Note positions of selected mineral compositions (Pl: plagioclase, Kf: K-feldspars, Mu: muscovite, Il: illite, Ka: kaolinite, Gi: gibbsite, Ch: chlorite, Sm: smectite).GAL: global average loess [1]; SED: average sedimentary rock [2]; UCC: upper continental crust [3].

The older type (Beremend Mb) of the TRCF is a red kaolinitic clay containing typically disordered kaolinite, mixed-layer smectite/kaolinite, smectite and little gibbsite. It was formed in a local subaerial weathering crust in warm, humid, subtropical or monsoon climate. The younger member (Tengelic Mb) of the TRCF contains red (or "reddish") clay beds. It contains relatively unaltered material (rich in illite, chlorite), the weathering products are predominantly smectite and goethite formed under warm and temporarily dry climatic conditions of savannah and steppe or forest steppe. The basal red clay layers of the PLF and KRCF contain similar minerals as the underlying red clays belonging to the younger member of the TRCF. The phyllosilicate assemblage (more illite and chlorite, less smectite) indicates a decreased rate of hydrolysis triggered by cooling and/or drying of the climate.

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Illite crystallinity and intensity ratio in the marine surface sediments around the Korean Peninsula

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Illite is the most abundant clay mineral in the marine surface sediments around the Korean Peninsula. We studied the mineralogical characteristics of illite such as Kübler index (KI) and intensity ratio (IR), using 33 surface sediments which were collected at Northwest Mudbelt deposit (NWMD, 17 samples), South Sea of Korea Mudbelt deposit (SSKMD, 3 samples), Hucksan Mudbelt deposit (HSMD, 2 samples) and Jeju Mudbelt deposit (JJMD, 11 samples).

Illite has very low KI (0.14-0.16) and wide range of IR (1.15-1.90) in the JJMD, medium to high KI (0.32-0.44) and IR (1.46-1.95) in the SSKMD and HSMD, and wide range of KI (0.28-0.58) and IR (1.08-1.70) in the NWMD (Fig. 1).

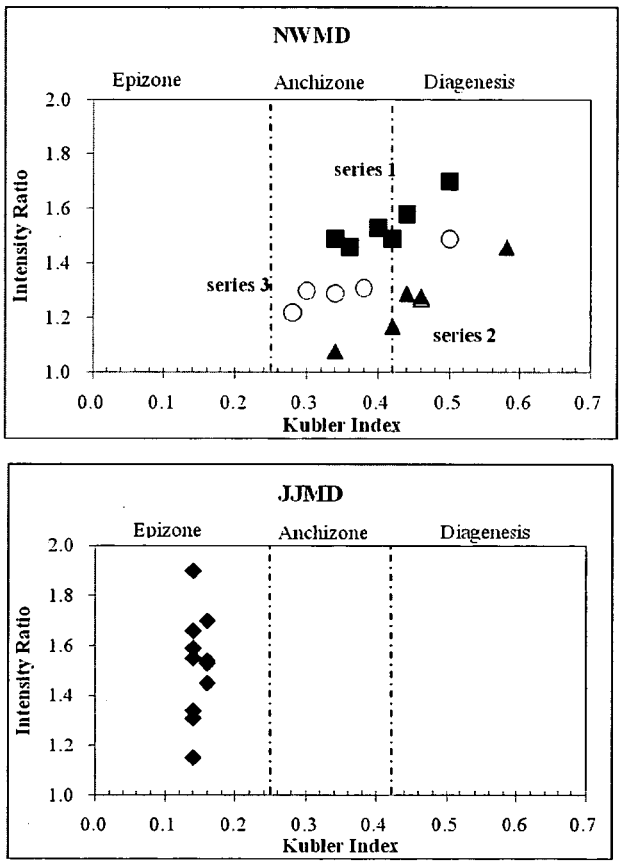

Fig. 1: Relationship between Kubler Index and Intensity Ratio at Northwest Mudbelt deposit (NWMD) and Jeju Mudbelt deposit (JJMD). Dashed lines are boundaries between each metamorphic zone after Kübler [1].

In the NWMD, KI and IR have positive relationship in the NWMD. Generally series 1 is distributed in eastern part, series 2 is in western part, and series 3 is in central part of NWMD. Each series might stand for different sediment provenance.

[1] Kübler, B. (1967) in Wegmann, C.E. (ed.) *Etages tectoniques*. Colloque de Neuchatel, Baconniere, 105-121.

Cretaceous-Paleogene boundary clay (Fish Clay) at Højerup (Stevns Klint, Denmark): Cu and Cr in the smectite concentrate

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The Fish Clay (of earliest Danian age) at Højerup belongs to one of the classic Cretaceous-Paleogene deposits at Stevns Klint. The main part of this sediment constitutes basal black marl. The mineralogy of the marl is comparatively simple, authigenic (mainly biogenic) calcite and detrital (Cheto-type) Mg-smectite being the principle components.

We report here a geochemical study of trace Cu and Cr in the inorganic (carbonate, smectite, silicate) fractions and in kerogen of the basal black marl. These metals were determined by inductively coupled plasma-optical emission spectroscopy in the whole rock sample, in the inorganic fractions and in kerogen.

Table 1: Geochemical data for Cu and Cr in the basal black marl

	Fraction*				
	Total	Carbonate	Smectite	Silicate	Kerogen
Concentration [ppm]					
Cu	80	10	160	15	715
Cr	150	20	350	15	160
Distribution [%]					
Cu	100	6	74	6	13
Cr	100	7	89	<3	<3

* Composition of the whole sample: carbonate [52.0 %], smectite [21 %], silicate [25.2 %], kerogen [1.8 %].

The analytical results show that geochemical concentrations of the Cu and Cr in the smectite concentrate is 160 and 350 ppm, respectively, and most of Cu and Cr reside in this fraction (Table 1). Substantial proportion of Cu is terrestrial and was probably contained in the detrital smectite arriving at the site of deposition. The predominant source of Cr was probably ejecta fallout deposited on the top of nearby coastal soil which was leached by impact-induced, possibly, acid surface waters. Most of Cr was derived from the chondritic component of the fallout. The incorporation of Cr into the smectite took place at the Cretaceous-Paleogene boundary, before the smectite redeposition to the Fish Clay site.

Composition and origin of the Barremian clay-rich sediments from the Mljet Island, Croatia

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Grayish-green clay and marl can be found in several localities on the island of Mljet (Dalmatia, Croatia) within the Lower Cretaceous shallow-water carbonate platform rocks. The clays and marls are usually present as thin irregular layers, couple of centimetres thick, but in some localities they build layers having thickness up to 2 metres. They were analyzed by X-ray diffraction, IR-spectroscopic, chemical and K-Ar dating methods in order to determine their composition and origin. Samples of limestones taken immediately below and above the clay layers were analysed by micropalaeontological and microfacies methods while their insoluble residues were analysed by X-ray diffraction method. This study focuses on major mineralogical observations.

The age of underlying limestones is Barremian, as indicated by their microfossil content (mainly dasycladacean algae). Microfacies analysis of some layers, classified as algal or peloidal-bioclastic wackestone-packstones, indicate shallow sea environment with low to medium energy. Some of them show possible remains of paleosol and mm to cm-sized cracks that could be produced by plant roots (rhizoliths). Limestones above clay layer, deposited in interdital/supratidal environment, classified as mudstone-wackestones, are micritic with cracks and fenestrae showing geopetal infilling and sometimes with stromatolites. The succession of deposits is composed of shallowing-upward cycles and the clays indicate emersion.

Minerals that were determined in the clay are illite, chlorite, kaolinite and calcite. Limestones sampled above the clay layer had 0.4-2.5wt.% of insoluble residue composed of illite, chlorite and kaolinite, which is very similar in composition to the clay samples. In addition some of them contain authigenic potassium feldspar. The mineral composition of insoluble residue, which accounts for 1.6 wt.% of the brecciated limestone underlying the clay layer, is dominated by muscovite, quartz and kaolinite, which is significantly different from that of clay.

The origin of clay cannot be determined unambiguously. Different mineral composition of clay and of the insoluble residue from the underlying limestone indicates that most likely clay is not derived from these limestones. It can be presumed that volcanic dust, possibly transported by wind from very distant areas, can be the source of the clay material, which is a result of volcanic dust weathering and subsequent diagenetic processes.

Interstratified chlorite/smectite minerals from some epithermal Au-Ag vein deposits in Japan, occurrence characteristics and chemical composition

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Interstratified chlorite/smectite minerals including corrensite occur widely in hydrothermal ore deposits [1]. The occurrence characteristics and mineralogical properties of chlorite/ smectite minerals are important in understanding the formation in hydrothermal environments and the usefulness of hydrothermal indicators in exploration for ores. The occurrence characteristics and chemical composition of the minerals from some Neogene epithermal Au-Ag vein deposits in Japan were investigated by XRD, optical microscopy, SEM, ATEM and EPMA.

The chlorite/smectite minerals are frequently observable as a vein mineral occurring in the ore veins and as an alteration mineral in the host rocks. In the former case it is characteristic that the minerals show microscopically banded or spotted shapes of aggregates in vein quartz, closely assembled with Au-Ag minerals and/or base metal sulphide minerals, and occasionally with manganese minerals. The chlorite/smectite minerals contain Mn in addition to the major octahedral cations (Mg, Fe). The Mn content of the minerals reflects the mineral assemblage, and the minerals assembled with rhodochrosite ($MnCO_3$) show higher Mn content than those without rhodochrosite. It is characteristic that grain by grain ATEM-analysis of the minerals shows a negative correlation of (Mn + Fe) vs. Mg. In addition, Mn/Fe ratios of the chlorite/smectite minerals vary in a wide range and positively correlate with the Mn/Fe ratios of coexisting sphalerite [(Zn, Fe, Mn)S]. As alteration mineral in the host rocks, spatial distribution of the chlorite/smectite minerals exhibits a close relationship with that of the Au-Ag ore veins [2].

These observations suggest that the interstratified chlorite/smectite minerals closely associated with the epithermal Au-Ag vein deposits have formed in and around the ore veins during the Au-Ag ore formation, and that the mineralogical properties of the minerals have been constrained by the hydrothermal conditions of the vein formation.

[1] Yoneda, T. & Watanabe, T. (1989) *Mining Geol.*, **39**,181-190. [2] Murata, K. et al. (2008) *Res. Geol.*, **58**, 111-119.

Geological, mineralogical and chemical characterization of kaolinite from Micaya, La Paz- Bolivia

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The aim of this study is to characterize clay deposits in the Micaya area located between the towns of Totorani and Colquencha, in the North Altiplano, Aroma Province, La Paz in Bolivia. This area was studied in order to enhance the knowledge of the local geology and to characterize kaolinite clay deposits identified within the Vila Vila formation. Geological mapping and chemical and mineralogical analytical techniques such as x-Ray Diffraction (XRD), Differential thermal analysis (DTA), Thermo-gravimetric Analysis (TG) and Induced Couple Plasma (ICP) have been used in this study.

In the Bolivian Altiplano, three main deposits of clays have been discovered, all of them used as construction materials [1]. The clay deposits are widely distributed in the country, and are derived from alteration and weathering of igneous and sedimentary rocks, transported and eventually deposited in the Tertiary and Quaternary sedimentary basins. The geologic mapping was performed in order to identify lithological and geological features, and clay samples from the Vila Vila Formation were collected for analysis and igneous samples for petrographic studies.

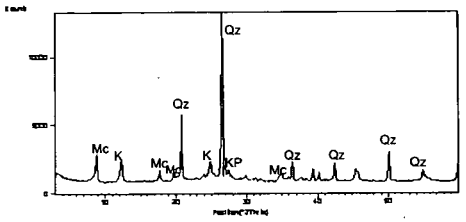

Fig. 1: Representative X-ray powder diffraction pattern of a sample from the Vila Vila Fm., showing the mineral assemblage.

In Figure 1, the XRD pattern of a representative sample from the Vila Vila formation is shown. Quartz is the major constituent showing a strong peak at 26,8° very characteristic of this phase, and is estimated semi-quantitatively as 56 wt.%. Muscovite is represented by a peak at 8,81° and estimated as 21 wt.%, kaolinite shows a peak at 12,3°, characteristic of this mineral phase [2] and corresponding to 18 wt.% and finally potassium feldspar, semi-quantitatively corresponds to 5 wt.%.

ICP analysis result confirms the XRD results with an SiO_2 content of 71wt.% and an Al_2O_3 content of 16,7wt.% for the same samples. DTA and TG analysis show an endothermic peak at 573°C related to the transformation of α-quartz to β-quartz and also an exotherm peak at 989, 1°C due to the phase change of kaolinite, when the hydroxyl (OH) groups are lost during heating.

This initial study shows that kaolinite is a major constituent of the Vila Vila Formation and could constitute a new important source of commercial kaolinite clay in Bolivia.

[1] Escobar-Diaz, A., Bellot-La Torre, J. & Jurado-Aramayo, E. (2000) *Bull. Natl. Serv. Geol. Mining*, **22**, 47-74. [2] Brown, G., & Brindley, G.W. (1980) in Brindley, G.W. & Brown, G. (eds.) Mineral. Soc. Monogr., **5**, 305-359.

Character of chlorite composition in Palaeo-Uplifts of Tarim Basin, China

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Chlorites are common in mudstones of the Mesozoic Formations in Palaeo-Uplifts of Tarim Basin, China. In order to study the chemical composition of chlorites, the authors collected samples systematically from different depths of bored wells. The rock samples were prepared as probe flakes. The chemical composition of was analyzed by EPMA. The analytical results are listed in Table 1.

Table 1: Results of EPMA measurements on chlorites

depth (m)	2777.4	3586.5	4405.3	5261.2
n	19	13	18	25
Al^{IV}	0.8839	1.0106	0.9880	0.9396
Al^{VI}	1.6384	1.7311	1.5581	1.6376
Si/Al	1.2462	1.0986	1.1906	1.1958
Fe/Fe+Mg	0.4551	0.5049	0.5340	0.5940
Ave.Temp (℃)	249.72	249.73	195.73	144.46

n: number of samples

The results show that in all cases the content of octahedral Al is greater than that of tetrahedral Al (Table 1), which suggests an authigenic origin and typical of what is found in other diagenetic chlorites [1,2]. The excess Al in the octahedral sites is due to the relatively high Si/Al ratio found in these authigenic chlorites (Table 1). The burial depth is strongly correlated with the Fe/Fe+Mg ratio of the chlorite. Using standard methods of geothermometry, for chlorite from the depth of 5261.2 m, a significantly lower crystallization temperature is estimated than for those from the shallower depths (Table 1). Using SEM, chlorite crystals appear together with NaCl grains except of the sample from the depth of 5261.2 m. Considering that other parameters (fO_2 and pH of the solution, coexisting mineral assemblages, and the bulk mineral composition of the host rock etc.) influence chlorite composition [3], an increased salinity indicated by the NaCl grains would be a major parameter influencing the composition of the chlorites in the area. The chemical analysis and the trace element data of rocks also show that the content of Na_2O is only 0.77 wt% in the rocks that does not contain NaCl grains , and the ratio of Sr/Ba is only 0.2; while the content of Na_2O is 1.14-2.29 wt% in the NaCl-rich rocks where the ratio of Sr/Ba is 0.4-5.7. These data can reflect the relative paleosalinity of the rocks. Because the salinities from the depths of 2777.4m and 3586.5m are higher than that of 4405.3m, thus it can be estimated the paleotemperatures are also higher. Furthermore, the paleotemperature from 5261.2m is the lowest since no NaCl grains can be observed at this depth. Therefore, chlorite geothermometry should be used with caution.

Acknowledgements: This work is supported by the National Natural Science Foundation of China (Project number 40772027).

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Influence of extrinsic factors on granite weathering in a glacier forefield

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Initial weathering processes and soil formation are of particular interest in alpine postglacial area due to their crucial role on life under harsh conditions [1]. At near-neutral pH under aerobic conditions, the availability of nutrients in fine-grained rock material and soil is usually very low. To overcome this limitation, microorganisms and plants modify their local environment by various exudates including organic ligands, siderophores and also cyanide, which is a very important agent during the initial period of colonization and soil formation.

We study mechanisms of weathering of primary rock-forming minerals in terms of intrinsic (e.g. mineralogy, surface area) and extrinsic weathering factors (e.g. pH, Eh, concentrations of ligands). Rocks and weathered stream sediments were obtained from the Damma glacier area (Central Alps, Switzerland) at approximately 2200 m.a.s.l.

Mineralogical composition determined by X-ray diffraction spectroscopy and Rietveld analysis shows homogeneity throughout the glacier forefield. Grain-size distribution is influenced by hydrological factors such as temporal availability and flow velocity of water. In the grain-size fraction <250 µm, the effect of weathering processes was observed from the loss of feldspar and biotite.

In addition to field observations, weathering of crushed granite is investigated in controlled lab experiments. At 25 °C, the influence of cyanide is studied in batch reactors as function of pH and ligand concentrations. The concentration of cyanide is maintained by a constant partial pressure of hydrogen cyanide through gas bubbling. Thus, the concentration of cyanide anion strictly depends on pH. Preliminary results show that the presence of cyanide leads to an increase in the mobilization of phosphorus and nutrient cations (e.g. calcium and magnesium).

[1] Bernasconi, S.M. et al. (2008) *Mineral Mag.*, **72**, 19-22.

Initial pedogenesis in a recently exposed Alpine proglacial area

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Climate change and glacier melting feed the need for understanding the processes related to weathering of recently exposed areas. Past studies in high Alpine environments show that clay mineral formation rates are higher in younger soils (<1000 yr) than in older soils (>10000 yr). However, investigations of processes that occur in the first decades of soil formation are rare.

In the present study we investigated the clay mineral formation in a recently exposed high Alpine chronosequence. The study was undertaken in the Morteratsch glacier forefield, located in SE Switzerland. The progressively exposed proglacial area offers a full time sequence from 0 to 150 yr old surfaces. The rock basement is the Bernina crystalline unit, a lithostratigraphic formation that is mostly constituted of Variscan granitoid rocks. Previous mineralogical studies carried out in the soils of the proglacial forefield [1] show a decrease of biotite and epidote as a function of time in the fine earth fraction (<2 mm). Mineralogical measurements of the clay fraction (<2 µm) were now carried out using XRD and DRIFT. The X-ray investigations included treatments of the clay fraction (Mg- and K-saturation, ethylene glycol solvation, heating at 335 and 550°C), a hot Na-citrate treatment to determine low-charged 2:1 clay minerals, whose expansion was hindered in the untreated state by interlayered polymers, and a layer charge estimation using alkylammonium (C18). Furthermore, analyses in the d(060) range were carried out. Decreasing content of trioctahedral phases with time in the clay fraction confirm active chemical weathering processes and formation and transformation mechanisms of parent rock mineralogy.

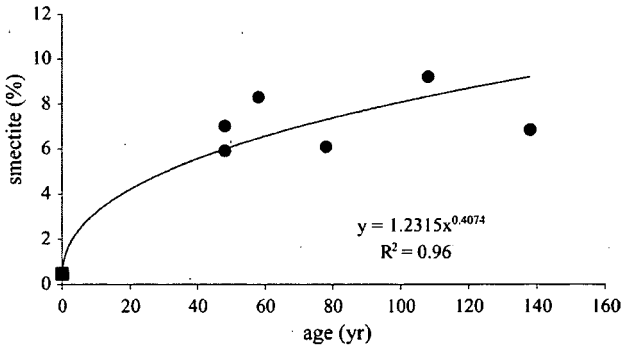

Fig. 1: Smectite formation as a function of time.

Smectite, having a charge of about 0.3 per half formula unit, was detected in a small amount already in the parent material. Along the selected chronosequence, smectite content increased steadily (Fig. 1). Hydroxy-interlayered smectites (HIS) were also present in the very early stages of soil formation and showed a weak increasing tendency with time. The clay mineral formation and transformation processes that are detectable already within a time span of 150 yr, confirm the high reaction rates of young areas in the glacier forefield.

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Weathering and pedogenesis from ultrabasic rocks (dunite-harzburgite complex) in bioclimatic conditions of mountainous tundra, the Polar Urals, Russia

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[3]Geological Faculty Moscow State University, Moscow, Russia

Ultrabasic rocks of the Rai-Iz massif, the Polar Urals (Russia) are represented by a dunite - harzburgite complex. Shallow Haplic Cryosols (Reductaquic) [1] are located in mountainous tundra where the permafrost is at a depth of ~ 30cm. Crushed stones and gravels of serpentinous dunites (olivine) are made up by ~ 70% of the total volume in sola. Olivine grains were broken into fragments; in veins, olivine may be replaced by serpentines, talc, and chlorites. Serpentine is also may be replaced by chlorite. Fragments of olivine, amphiboles, chlorites, serpentine, and pyroxenes are frequent in thin sections of soil horizons. Source of pyroxenes are harzburgite.

Mineral identification and swelling properties of minerals were studied in fine size fractions (<1μm and 1-5μm) by a complex of methods: thermal analysis, infrared spectroscopy, scanning electron microscopy, and X-Ray diffraction (XRD) in natural disordered state and oriented mono-cationic forms (Mg, Li, K) - air-dried, ethylene glycol solvated and heated at 550°C during 2 hours.

The studied solum (loamy - clayey loamy) is pH- neutral in the upper and alkaline in the basal horizons keeping by high amounts of exchangeable Mg. In fine size fractions of sola inherited serpentine (chrysotile), talc, and chlorite are identified as well as pedogenic minerals [2]. Pedogenic minerals that are appeared in solum and are absent in rock, are represented by smectite and vermiculite. These minerals are characterised by different distribution in solum. Smectite is present in the bottom (Bgf) horizon as well as in the upper (Ah) where its content decreases. Vermiculite is identified only in the upper horizons of solum. This distribution could be a result of the acidic effect of moss and lichens despite the pH value of bulk samples. The acidic effect is the cause of: (i) selective decomposition of smectite as the most unstable minerals in acid conditions; and (ii) vermiculite appearance as a result of chlorite transformation. The intensity of processes (smectite decomposition and chlorite transformation) increases probably due to permafrost influence leading to pronounced rock disintegration and rise of their dispersion as a consequence of stability of inherited silicates.

Acknowledgements: This work was supported by Russian Foundation for Basic Research, project 09-05-00302 and 10-05-00300.

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Clay mineralogy and organo-mineral associations of Carboniferous paleosols (Moscow region, Russia)

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Lower Carboniferous (Missisipian) and Upper Carboniferous (Pennsylvanian) cyclothems and subaerial unconformities of the Moscow Basin contain abundant paleosols [1]. Here we report the properties of two Lower Carboniferous (334-326 My) and Late Carboniferous (308±2 My) paleosols which were obtained by means of the following methods: XRD, XRF, HCNS, FTIR and solid-state CP/MAS ^{13}C – NMR. Additionally chemical OM fractionation has been done [2].

For Holocene paleosols organic matter (OM) mineralization results in the organic carbon (OC) loss which reaches 50-70% after several hundred years after burial. More ancient paleosols as a rule contain only traces of OC (<1%), which is predominantly concentrated in their clay fraction [3]. OM transformation in paleosols includes not only quantitative but also the compositional changes and the increasing of humic acids and aromatic component is documented

Both Missisipian paleosols were formed under (semi) humid climate. They are smectitic, where beidellite (Profile 1) and saponite (Profile 2) predominate. OC content in their clay fraction is 1.2% and 0.5% respectively. Humic acids dominate in both profiles (C_{HA}/C_{FA} = 1.23-1.53). Humin content is 45% in Profile 1 and 18% in Profile 2. ^{13}C – NMR spectra are very similar and simple with the absolute predominance of aromatic component (60-64%).

Pennsylvanian (semi)arid paleosol is palygorskitic. Its clay fraction contains 1.1 - 1.5% of OC where fulvic acids visibly predominate (C_{HA}/C_{FA} = 0.55). ^{13}C – NMR spectra show the presence of well resolved peaks of alkyl-, aromatic carbon and polysaccharides (30 : 30 : 30%).

Basing on data obtained we suppose that OC content and composition of paleosols depends not only on pedogenesis, age and conditions after burial but also on the mechanisms of OM protection. These mechanisms are determined by the mineralogical composition and interactions between mineral matrix and organic molecules. In case of Pennsylvanian (semi)arid paleosol the labile organic compounds (polysaccharides) were stabilized by palygorskite matrices to a similar extent as humic compounds and both showed the resistance against mineralization for a period more than 300 My. The remarkable preservation of fulvic type of humus is related to formation of organo-mineral derivate where organic molecules are chemically bound to palygorskite lattice [3].

[1] Kabanov, P.B. et al. (2010) *J. Sedim. Res.*, **80** (in press). [2] Ponomareva, V.V. & Plotnikova, T.A. (1980) *Humic Substances and Soil Formation.* Nauka, Leningrad. [3] Alekseeva, T.V. et al. (2009) *Dokl. Biol. Sci.*, **425**, 128-132.

Holocene climate dynamic and biogeochemistry of palaeosols

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Palaeosols can act as integrative records of past climatic, lithological, geochemical, biological, and hydrological conditions. Kurgans in Russian steppe were constructed at different times from the mid-Holocene onwards; they preserve a range of palaeosols recording past environmental changes through this whole interval. Applying a soil magnetism climofunction, calculated from a modern day soil training set, to each set of buried soils enables quantitative estimation of precipitation at each time step when soil burial occurred [1].

The present study was related to the soil biogeochemical processes in connection with climate variation and duration of weathering. XRF analysis for bulk, clay and course fractions of palaeosols samples were done. Mass balance was used to differentiate between pedogenic processes and sources of elemental additions and losses. Considerable changes in the clay and iron oxide mineralogy, molar chemical ratios of the soils permit us to assess the rates of the mineralogical transformations caused by the climate dynamics in the interval of the last 5000 years. A change in soil mineralogy and as a consequence of the transformation of the chemical composition of the buried soils testifies the primary importance of climate factors in comparison with the total duration of the weathering process.

The relationship of ratio of Rb in humus horizon to the background concentration with climatic changes was observed. In soil, the behavior of Rb is controlled mainly by adsorption on clay minerals and organic matter.

The median Rb content is 60 mg kg^{-1} in subsoil and 80.0 mg kg^{-1} in topsoil; with increase in clay fraction up to 150 mg kg^{-1} in topsoil .The average ratio topsoil/subsoil is 1.45 for bulk samples, and 1.27 for clay fraction. The decrease of the K:Rb in the progressive development of soil observed. Plants use K, whereas Rb is not a biologically important cation, so the difference between the two represents pedogenesis development in our case with variability of climate.

[1] Alekseeva, T. et al. (2007) *Palaeogeogr. Palaeocl. Palaeoec.*, **249**, 103-127.

Clay minerals and humic acids in European paleosoils

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Soil characteristics of loess-paleosoil sequences reflect the changes of climate and vegetation during past glacial/interglacial cycles. Clay minerals, soil organic matter and carbonate content are indicators of weathering intensity and pedogenesis [1-3]. In warm periods kaolinite and poorly crystallized expandable minerals like smectite and vermiculite were formed, in cold periods enrichment in better crystallized illites, chlorites and feldspars occurred. The composition and structure of humus substances also reflect the climatic and ecological conditions during the time of their formation [4].

Different loess-paleosoil sequences from Wolkersdorf, Krems and Niederabsdorf (Lower Austria) and Dolni Vestonice (Czech Republic) were studied.

The mineralogical composition (bulk sample and clay fraction <2μm) was determined using X-ray diffraction. Dominating clay minerals in samples from all sites are chlorite, illite, and smectite, in some of the samples considerable amounts of vermiculite were found.

Soil analyses included chemical parameters like pH-value, electrical conductivity, total carbon and nitrogen, C/N-ratio, carbonate content and cation exchange capacity of the fine soil fractions. The CEC of the clay fraction was also determined. Grain size analyses were made by a combination of wet sieving and sedimentation.

Humic acids of the paleosoil samples were extracted using 1M NaOH and characterized using thermogravimetry, differential scanning calorimetry, Fourier transform infrared (FT-IR) spectroscopy and mass spectroscopy.

[1] Bajnóczi, B. et al. (2006) *Geophys. Res. Abst.*, **8**, 05228. [2] Karlstrom, E.T. et al. (2008) *Catena*, **72**, 113-128. [3] Vancampenhout, K. et al. (2008) *Quatern. Res.*, **69**, 145-162. [4] Dergacheva, M. (2003) *Quatern. Int.*, **106-107**, 73-78.

Sorption of copper on the eluviaton and accumulation horizons of a brown forest soil

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In this study copper immobilization ability in high ionic strength NaCl solution and at acidic pH is examined by comparing the sorption properties of two distinct soil horizons within one profile. The adsorption experiments were carried out on the well distinguishable eluviation and accumulation horizons of a brown forest soil, one of the dominating soil types in Hungary.

The eluviation (E) and accumulation (B_1) horizons of the studied soil profile differ from each other in their mineral composition and clay mineral characteristics. The clay mineral content of B_1 horizon is 30% larger than that of E horizon. According to the XRD studies two major clay mineral phases were distinguishable in the samples: a swelling interstratified chlorite/vermiculite in the B_1 horizon, and a non-swelling, probably hydroxy-interlayered vermiculite in the E horizon.

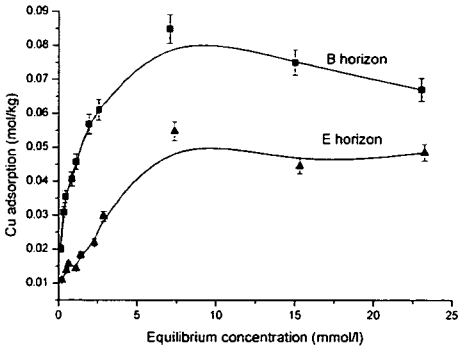

Fig. 1: Cu adsorption isotherms for B and E horizons.

The maximum copper adsorption calculated by Langmuir equation was 0.052 mol/kg Cu (3 304 mg/kg Cu) for the E horizon, and 0.071 mol/kg (4 512 mg/kg) Cu for the B horizon (Fig. 1). The differences arise from the different mineral composition of the distinct horizons. Hydrous iron oxides and swelling chlorite/vermiculite in the accumulation layer increase Cu adsorption capacity, while hydroxy-interlayering in vermiculite, and absence of iron oxides decrease Cu uptake of the eluviated horizon. Based on XRD studies, measurable fraction of Cu was sorbed in the interlayer space of vermiculite by ion exchange mechanism. This sorbed Cu caused the loss of expansion capacity of the vermiculite.

Our study of Cu adsorption on the eluviation and accumulation horizon of a brown forest soil confirmed that the different genetic layers in a soil profile can play different role in the immobilization of heavy metal contaminations.

A K/Ar study of structural and chemical changes of < 2 μm-sized minerals from fertilized soils

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K/Ar dating is based on the measurement of radiogenic ^{40}Ar isotope formed by the radioactive decay of ^{40}K. The K/Ar clock starts (1) at the time of mineral formation, if this happens below the so called „closure temperature", or (2) when it cools below its closure temperature. Diagenesis and low grade metamorphism is dated mostly by K/Ar method using < 2 μm-sized minerals. Difficulties of interpretation of age data have been reviewed recently [1].

During erosion, transportation and deposition clay minerals retain their K/Ar age. The formal age of clay minerals of the Hungarian Plain is mostly Mesozoic. The influence of fertilizers on the structure and chemistry of clay minerals are summarized in [1]. Research of clay mineral transformations in fertilized soils is in progress in Hungary since the 70's [2,3].

During structural change the possible escape of $^{40}Ar(rad)$ and incorporation of K decrease the K/Ar "age". The samples are taken from soils treated with variable doses of N, P and K fertilizers for 35 years (Table 1). The site of the study is Nagyhörcsök, with calcareous chernozem loamy soil (20-23% clay, 5% $CaCO_3$, 3% humus in the upper 0-30 cm layer). The groundwater table was at a depth of 13-15 m, the water balance of the site was negative. The K-balance was between –2.4 and +4.9 t/ha at the end of the 35 years of the field trial. The NH_4-acetate + EDTA soluble K-content (column 3 in Table 1) showed K-deficiency and high K-supply of the plots.

Table 1: K/Ar ages of clay minerals in NPK treated soils

No.	*N*	*P*	*K*	*(1)*	*(2)*	*(3)*	*(K%)*	*Age±σ My*
1	0	0	0.00	1.88	-1.88	145	2.340	123.6±4.8
2	0	0	2.07	2.48	-0.41	235	2.542	115.1±3.6
3	0	0	4.15	2.67	+1.48	285	2.503	121.0±3.9
4	0	0	6.22	2.78	+3.44	407	2.679	115.7±3.7
5	1	0	2.08	3.47	-1.39	149	2.482	132.4±5.2
6	1	0	4.15	3.80	+0.35	197	2.443	130.9±5.1
7	1	0	6.22	4.22	+2.00	354	2.622	119.5±4.6
8	2	4	0.00	2.44	-2.44	94	2.193	127.4±5.1
9	2	5	0.00	2.00	-2.00	117	2.305	133.0±5.1
10	2	5	7.06	2.15	+4.91	754	2.975	107.5±4.2
11	2	5	7.06	2.35	+4.71	701	2.806	110.2±4.4

Given fertilizers: N0=0, N1=100, N2=200kg/ha/year (N dose); P0=0, P4=50, P5=100 kg/ha/year (P_2O_5 dose); K: t/ha/35years; (1): K uptake by plants in t/ha/35years; (2): K-balance in t/ha/35years; (3) K/soil (mg/kg); K%: in dated mineral

Data in Table 1 show that adding K decreases while N increases the "age". K added by fertilizers and trans-ported by the vegetation change the "age" similarly.

[1] Meunier, A. & Velde, B. (2004) *Illite.* Springer, Berlin-Heidelberg-N.Y. [2] Varjú, E.M. & Stefanovits, P. (1979) In: Mortland, M.M. & Farmer, V.C. (eds.) *Develop. Sedimentol.*, **27**, 349-358. [3] Rózsavölgyi, J., Kádár, I. & Sarkadi, J. (1986) *Növénytermesztés,* **35**, 325-331.

Clay mineralogy of the nickel laterite profiles associated with the Western Vardar ophiolite zone

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Two laterite profiles associated with the Western Vardar ophiolite zone have been investigated in order to estimate the formation conditions of the secondary minerals and the trace element behaviour during tropical weathering of serpentinite from the ophiolitic complex.

Nickel laterite deposit in the village Ba (44.15°N, 20.20°E), Serbia, has been formed by the weathering of serpentinite thrust over the Triassic limestone. The weathering of serpentinite in karstic environment produced a number of nickel-bearing minerals including nickeliferous clay minerals [1]. According to X-ray powder diffraction (XRPD) analysis the principal clay mineral is montmorillonite with cation exchange capacity (CEC) in the range between 70 and 73 mEq/100g. Gibbsite and minor amount of 7Å-halloysite occur as well.

The Ni-laterite weathering crust at Gornje Orešje locality (46.01°N, 16.22°E), Croatia, comprises, from the base up, the bed rocks (serpentinized harzburgite, massive apoharzburgitic serpentinite, apodunitic serpentine and schistose serpentinite); the saprolite zone (highly fractured and oxidized serpentinite) and the clayey zone [2]. Montmorillonite represents the most dominant clay mineral.

The following reaction illustrates the breakdown of serpentine (lizardite) into Mg-montmorillonite:

$$11\ Mg_3Si_2O_5(OH)_4 + 14\ Al^{3+} + 22\ H^+ \leftrightarrow$$
$$6\ [Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2]Mg_{0.167} + 32\ Mg^{2+} + 27\ H_2O$$

Logarithmic activity diagram, constructed for standard conditions (p= 1 bar, t =25°C) according to thermodynamic data published by [3] and [4], indicates stability of montmorillonite at $log\ a(Al^{3+})/\ a(H^+)^3$ and $log\ a(Mg^{2+})/\ a(H^+)^2$ above 10 and 0, respectively (Fig. 1). Mobility of aluminium in form of Al^{3+} required decreased pH ($a(Al) = 10^{-6}$; pH < 4.4).

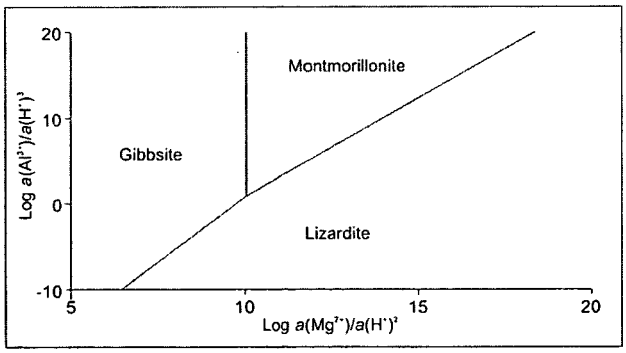

Fig. 1: Stability of Mg-montmorillonite, gibbsite and lizardite (p=1 bar; t=25°C).

[1] Maksimović, Z. (2004) *Bull. Acad. Serbe Sci. Arts. Classe Sci. Nat. Math., Sci. Nat.*, **42**, 342-361. [2] Palinkaš, L.A. et al. (2006) in Gerzina, N. & Resimić-Šarić, K. (eds.) *Mesozoic Ophiolite Belts of the Northern part of the Balkan Peninsula – Ophiolites.* Faculty of Mining and Geology, Belgrade, 97-101. [3] Woods, T.L. & Garrels, R.M. (1987) *Thermodynamic values at low temperature for natural inorganic materials.* Oxford University Press, New York. [4] Brookins, D.G. (1988) *Eh-pH diagrams for geochemistry.* Springer-Verlag, Berlin.

Clay mineral alterations in a chronosequence of podzols on Alnö Island, Sweden

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Chronosequences are potent instruments for pedological investigations and testing pedological theories. Chronosequences are especially useful for soils that have developed on surfaces of known age, e. g. moraines, alluvial fans and terraces, lava flows and coastal sand dunes. Since the highest elevation above sea level on Alnö is 128 m at present, it was calculated that the emergence must have taken place between 7400 and 7700 years BP. As this is at the same time the beginning of terrestrial soil formation, the oldest soils on the island are subsequently between 7400 and 7700 years old. By considering the uplift of the land and the development of the shoreline, the age of a soil at a certain elevation above sea level can be determined.

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When studying soils, the examination of clay minerals is essential for determining their physical and chemical properties, as clays are often highly reactive. Clay minerals are useful for former and current weathering processes, because the weathering intensity depends on the contact area of the mineral particles and the liquid phase. It has been shown, that the rate of chemical weathering increases with decreasing particle size. The formation of clay minerals depends upon physicochemical conditions, parent material and environmental factors. Clay minerals in podzols are often formed by acidolysis, which occurs when the pH is lower than 5. The dominant clay minerals then are smectites, vermiculites, Al-intergrades and Al-chlorites.

The focus of the project is to elucidate the processes of pedogenesis in the Holocene from a clay mineralogical point of view. As clay minerals are sensitive to changes of their environment, they can be used as indicators for soil development during pedogenesis and, subsequently, as indicators for the soil age. The results of the clay mineralogical analyses and of the assessment regarding the applicability of the clay mineral distribution as relative dating method for soils, will be presented.

The effect of electrolytes on the surface layer formation of a basaltic glass

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Volcanic glasses, produced every year in high amounts by rapid cooling of magma, play an important role in the global and local cycling of numerous elements. The dissolution rates of natural glasses are affected by the composition of the surrounding solution. In presence of aqueous species that lead to the formation of Al-complexes, the dissolution rate of basaltic glass will increase [1]. In this study the zeta potential is used to determine the effect of different anions and cations on the surface layer formation of a basaltic glass.

Experiments were performed with a powder of a synthetic basalt glass with typical MORB composition, which has a mean particle size of 1.9 µm and a specific surface area of 1.7 m^2/g. For determination of electrolyte effects (e.g. NaCl, NaF, $Na_2C_2O_4$, Na_2SO_4, $Ca(NO_3)_2$, $Al(NO_3)_3$) on the zeta potential with time, 100 mg of sample were added to 200 ml of the solutions in the concentration range of 0.0001 to 0.005 mol/L. The zeta potential was determined together with the electrical conductivity of the solution (Zeta PALS, BIC).

The presence of F in the suspension resulted in a decrease of the zeta potential, indicating the adsorption of F on the surface of the basaltic glass (Fig. 1). This trend is strengthened at higher F concentrations indicating more extensive F adsorption. For non adsorbing electrolytes at higher ionic strength an increase of the zeta potential by the compression of the diffuse double layer is observed.

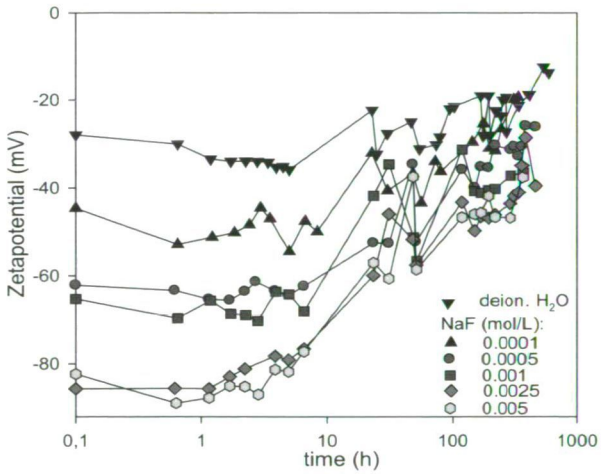

Fig. 1: Effect of NaF on the zeta potential of a basaltic glass in the time period up to 600 h.

With time zeta potential is increasing for all suspensions indicating that most probably Al and Fe in the surface layer are enriched. By the addition of divalent cations together with weakly adsorbing monovalent anions the point of zero charge is reached within the time period of 600 h at slightly acidic pH-values. Here a decrease in the dissolution rate can be assumed which is determined in currently running long term dissolution experiments.

[1] Wolff-Boenisch, D. et al. (2004) *Geochim. Cosmochim. Ac.*, **68**, 4571-4582.

SEM analysis of slickenside surfaces of smectitic soils of Hungary

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Smectitic soils develop special morphological characteristics under alternate wet-dry conditions determined by swelling pressure, occurring when the swelling clays adsorb water. The dilation of clays during hydration generates an abiotic stress resulting in special morphological features like slickensides [1], and also determines fertility, soil management practises and the success of crop production. These unique smectitic soils are classified as Vertisols according to the modern soil classification systems.

The slickensides, the most characteristic Vertisol phenomena, are polished and shiny ped surfaces, produced by one mass of soil sliding past another to relieve the stress generated by the swelling pressure. Surface characteristics of slickensides from a Vertisol of Kisújszállás, Hungary were studied on fractured, undisturbed blocks with planar orientation by Hitachi S-4700 scanning electron microscope.

The SEM analysis of the slickenside surfaces showed differences from the subjacent micromass of the ped interiors with stronger preferred orientation of clay particles, and increase in micropores. Micro-grooves approximately 4 to 20 µm wide (Fig. 1a) were detected according to the direction of the sliding, developed due to plastic deformation, or sand grains translated parallel to the direction of the shear failure. The stress reoriented clay particles resulted in a "face to face" clay alignment on surfaces of slickensides (Fig. 1b)

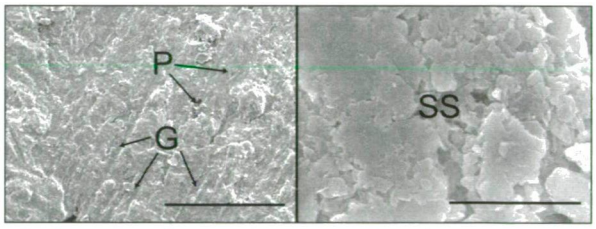

Fig. 1: Scanning electron microphotographs of slickenside surfaces (planar view) of Vertisol of Kisújszállás a) showing grooving (G) and pores (P) (bar length is 300 µm), and b) oriented clay on surface of the slickenside (SS) (bar length is 5 µm).

The presence of an oriented clay layer had direct impact on the orientation and size distribution of pores and cracks also. The presence of stress oriented clay features was resulted in smaller pore size and on slickenside surfaces. Based on the SEM analysis of the slickenside surface of the Kisújszállás Vertisol, the slickenside had pores that were generally less than 7 µm in diameter (Fig. 1a).

These characteristics could make slickensides act as semi-permeable barriers to solute transport, and effect hydrological, and chemical properties of Vertisols, determining agricultural and engineering use also. Thus the knowledge on morphology is essential to be able to make right decisions on suitable management.

[1] Wilding, L.P. & Tessier, D. (1988) in Wilding, L.P. & Puentes, R. (eds.) *Vertisols: Their Distribution, Properties, Classification and Management*. Tech. Mono., **18**, A&M Printing Center, College Station, Texas, 55-79.

Comparison of clay minerals in soils derived from basalts and phonolites under temperate climate of Lower Silesia, Poland

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Our study included six soil profiles derived from basalts and phonolites. Each rock was represented by 3 soil profiles. Objects were located in the Sudetes in the Lower Silesia Region, Poland (Fig. 1.). The investigated area lies under temperate climate, with temperatures 7-8.5°C and rainfalls of 650-700 mm. Soil samples were collected in upper parts of the old quarries, at elevation of 250 – 330 m a.s.l. Such approach allowed us to investigate only the effects of parent rock composition on soil properties and weathering products, and to eliminate effects of other soil forming processes. Analyzed soils represent cambisols with shallow profile. Soil samples in this study were collected from the top (A) and parent rock horizons (C) of each profile in order to determine possible differences in clay mineral composition.

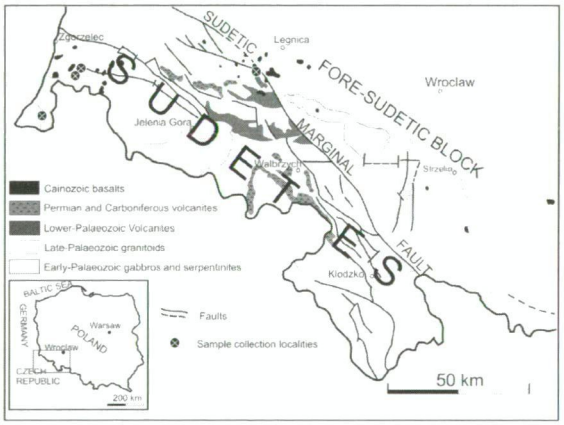

Fig. 1: Sitemap with location of sampling (based on Przybylski [1]).

The clay minerals in each sample were characterized by means of X-ray diffraction patterns and different proportions of clay minerals were observed in phonolites and basalts and also between different basalt types. Kaolinite and illite occur in all studied samples. In soils developed from phonolites kaolinite dominates, illite occurs only in small amounts and vermiculite amount is very low. It is consistent with kaolinite being the main weathering product of K-feldspar and feldspatoids, which are major components of phonolites.

Vermiculite is the dominant clay mineral in two of the investigated basalt derived profiles. Basalt, as a rock rich in Mg- and Fe-, should generally show presence of vermiculite in colloidal fractions in soils under temperate climate. In addition to vermiculite, XRD patterns revealed the presence of kaolinite and illite in the studied samples. In some profiles small amounts of smectites were also observed.

The results of our study showed that, under the temperate climate, weathering products of rocks largely depend on the original mineral composition of the parent rock.

[1] Przybylski, T.A. (2004) *J. Environ. Radioactiv.*, 75, 171-191.

The influence of clay on site characteristics in the Vienna Forest, Austria

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The Vienna forest is situated in the very east of the Alps, on the western border of the Tertiary Vienna Basin. Covering 1,350 km^2, it is an important local recreation area for Viennese people and also serves as "Green Lung" for the City. In 2005, the Vienna Forest was also designated a Biosphere Reserve by UNESCO.

From Pleistocene till recent days the river Danube is still forming the landscape of the surroundings of Vienna. The following geological classification can be done:

- Gravel and sand from the Danube from Pleistocene till today
- Fine grained sediments like marls from Tertiary time in the Vienna Basin
- Sandstones from the Flysch zone and limestones from the Calcareous Alps
- Red marls – also named "Red Loams" - from the „Klippenzone" of the Ultrahelvetikum

During construction works in the western districts of Vienna (16th, 17th, 18th) extraordinary red loams from the above mentioned "Klippenzone" emerged. In parts of the Vienna forest these red loams are parent material for the pedogenesis.

The term „Red Loam" is generally - and colloquially - used for red soils and comprises Kalkrotlehme and Kalkbraunlehme according to the Austrian Soil Classification System as well as red marls.

Red marls are „Farb-Substratböden". Typical for those types of soil is that the profile of the soil is very much characterized by the colour of the parent material and the genetic differentiation of horizons is hidden. „Kalklehme" are very clayey soils coloured brown to red and developed from the residual material of weathered limestone.

By means of bulk and clay mineral analysis with XRD, STA, FTIR, grain size and further chemical analyses the amount and type of clay minerals in the soils will be characterized. The determined parameters are important for the water and nutrient regime of the forest soils.

The results of bulk and clay mineral analysis done by XRD show unexpected results. The content of clay is very high and reaches from 40 to 60 percent in the investigated samples. Some of them show high amounts of smectite and soil vermiculite and some contain illite and chlorite as well. Although the investigation sites are situated closely to each other, the mineralogical composition of the soils varies and shows different levels of weathering, which is a clear indicator for solifluction processes during the Pleistocene.

Organo - metal and organic matter characteristics of clays from East Maritza Coal Basin (Bulgaria)

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Ten core samples of Miocene black clays from two boreholes (East Maritza Coal Basin, Bulgaria) were characterised by their grain-size distribution, whole rock mineralogy and organic geochemistry. Organic matter composition and type were determined using modified method of Tyurin and Kononova [1,2] based on three extractions with: (1) mixed solution of 0.1 M $Na_4P_2O_7$ and 0.1 N NaOH; (2) 0.1 N NaOH; (3) 0.1 N H_2SO_4. Five fractions were received: 1-pyrophosphate, 2-basic, 3-acidic, i.e. fulvic acids (FA) aggressive fraction, 4-humic acids (HA) total, 5-HA free and/or bound to three valence cations. Humic acids optical characteristics were measured on SPECOL (absorption at λ 465 nm and 665 nm). Zinc and Al content in organo-metal complexes in the extractions were analyzed by means of ICP-OEM.

According to the textural characteristics the clayey sediments are mainly claystones (rarely clayshales) with sandy and silty admixtures up to 30%. Mixed-layered illite/smectite mainly, and kaolinite are the predominant clay minerals. Small amount of quartz and feldspar admixtures were also detected.

The samples studied differ considerably in their total organic carbon (Corg) content (the data fall in the range of 1.21-15.08 %) and do not show any dependence with depth. Non-extracted C_{org} varies from 66.89 to 88.43 %. According to the ratio C_{org} in HA to C_{org} in FA, organic matter is of a humic type in four samples, humic-fulvic - in three, fulvic - in two; and fulvic-humic - in one. In one sample HA were not extracted at all. Humic acids are bound mainly to alkaline earth ions (over 50%) in 7 samples. In two samples only, more than 50% of HA are free and/or bond to three valence cations. Very low content of the aggressive FA fraction (0.1 N H_2SO_4 extract) is characteristic for all samples studied - 0.30-1.61 % of C_{org}. The optical characteristics show that most of the HA are low molecular, low condensed ones, with high values of E_4/E_6 ratio. In three samples E_4/E_6 values vary from 2.16 to 2.74 that probably corresponds to more condensed aromatic cores of their HA.

Aluminium and Zn distribution in all fractions extracted varies irregularly, in a wide range, and independently with the depth. High mean Al values were measured for the pyrophosphate and FA aggressive fraction extracts, and low - for HA free and/or bond to three valence cations. The highest mean Zn values were detected for FA aggressive fractions, and the lowest - for the alkaline fractions. There is one sample (C_{org} - 13.33%) where maximum Al values for pyrophosphate, total and free/or three valences bound HA were measured. In another one (C_{org} - 15.08%) were detected maximum Zn values for basic extracts, HA total, and HA free /or bound to three valence cations.

Based on the result obtained one could suggest that Al in samples studied is bound mainly to HAs whereas Zn is bound mainly to FAs aggressive fraction. It could be also concluded that East Maritza Coal Basin black clays possess presumably low potential for mobile organo-metal complexes generation because the HA are bound mainly to alkaline earth ions.

Acknowledgements: The study is a part of project VU-11/06 financed by NSF, MES, Sofia, Bulgaria.

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Changes of mineralogical paleoproxy indicators in a Quaternary loess–paleosol section at Beremend, Hungary

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Weathering strongly affects mineralogy of sediments including loess deposits with intervening paleosols. A variety of semiquantitative tools has been developed to examine past weathering and pedogenesis, and to reconstruct both paleoenvironmental and paleoclimatic conditions at the time of paleosol formation.

In this study, mineralogical composition was analyzed on loess and paleosol samples from SE Transdanubia, Villány Hills, Hungary. The studied Beremend section represents the Old Loess Series (OLS; ~380–700? ka; Marine Isotope Stage (MIS) 11–17?) and partially the Young Loess Series (YLS; ~130–250? ka; MIS 5–7?) exposing three reddish brown forest soils (Be-S1, Be-S2, Be-S3; OLS) and a brown forest or forest steppe soil (Be-S4; YLS). Unconformities among sediments appear to be common.

The bulk mineral composition of sediments estimated from XRD data indicates that quartz and smectite are the dominant minerals. Interestingly, throughout both the loess and paleosol units, relative proportion of quartz shows no variation. Loess samples contain high amounts of calcite; additionally, dolomite occurs in all loess samples and in the Be-S4 samples. Illitic material together with chlorite is present in all samples but usually in small proportion. Albite, K-feldspar, kaolinite, and goethite are the typical minor components with amorphous material. Aragonite is present only in a single loess sample.

In the clay fraction of the sediments, varying amounts of smectite, illite, chlorite, and kaolinite are present. Paleosol samples can be characterized as smectite-rich compared to loess samples which contain higher amounts of illite. The entire section shows no obvious variation in kaolinite content. Chlorite content is generally low, and slightly decreases upwards.

The quartz-normalized bulk kaolinite content shows systematic variations with lithology, especially in the lower and middle part of the Beremend section (corresponding to OLS). The bulk kaolinite/quartz ratio increases upwards in loess horizons, whereas it decreases in paleosol layers. As a paleoproxy indicator, changes in bulk kaolinite/illite ratio (K/I) show significant differences between the Beremend paleosol (K/I > 1) and loess (K/I < 1) samples suggesting fluctuations in the intensity of coeval continental hydrolysis. Based on clay mineralogy, the same stratigraphic pattern in the K/I ratio is apparent. In the lower and middle parts of the section (OLS), however, the K/I ratios in paleosols are significantly higher than those of fossil soil Be-S4 (YLS). Synchronous changes in the values of smectite/illite (S/I), smectite/(illite+chlorite) (S/I+C), and smectite/kaolinite (S/K) ratios are also observed.

The relatively higher S/I, S/(I+C), and S/K ratios, observed in paleosols, suggest a strengthened chemical weathering and weak physical erosion. By contrast, lower ratios in loesses, corresponding to glacial periods, indicate intensified physical erosion and weakened chemical weathering. Fluctuation of erosion rate is also supported by variations of bulk kaolinite/quartz ratio. Significantly lower values of mineralogical proxy indicators in the upper part of the Beremend section, corresponding to the YLS, may indicate a climate deterioriation with decreasing rates in continental erosion and chemical weathering from the OLS to YLS in SE Transdanubia.

Origin of aluminium from salt efflorescence on sandstone exposures

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Detailed study of salt efflorescence composition in many sandstone castellated rocks in the Middle Europe shows presence of Al-sulphates (alums), mostly on sandstone with clay sandstone matrix.

Isotopic composition confirmed the atmospheric origin of the salt efflorescence [1], but precipitation contains no aluminium [2]. Research in the sandstones of the Northwest Bohemia showed that sandstone vadose water may contain elevated concentrations of Al, Zn, and Cd [3].

Therefore, formation of alums can be explained by the partial dissolution of clay minerals or feldspars present in the sandstone matrix. Release of aluminium from these phases is facilitated by the low pH of the precipitation (pH 4–5) and also locally by organic acids, traces of which were found in the studied efflorescence by the use of infrared spectroscopy [1].

We studied several waters from vadose zone of sandstone and soil waters in one protected landscape area (PLA) from the Northern Bohemia (Czech Republic). Chemical composition of studied waters proved elevated content of aluminium, silica and few other ions compared to precipitation composition normalized to ET enrichment [4].

Study demonstrated that aluminium can be released from clay sandstone matrix (clay minerals or feldspars) or soil cover of sandstone. Presence of alums and other Al containing salt efflorescence is thus valuable indicator of vadose zone acidification, for example in Northern Bohemia.

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The study of clay minerals from the granitoids soils developed in a temperate climate

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Eight shallow soil profiles developed from different granitoids (leucogranite, granite, granodiorite and tonalite) were investigated, two from each rock type. The soil profiles were located in the Fore-Sudetic Block and the Sudetes, Lower Silesia, Poland (Fig. 1). To investigate only relationships between clay mineral and parent rock composition, and to avoid the effects of other soil forming factors, the profiles were located only on the top parts of hills 169 – 433 m a.s.l. and in similar climatic conditions, including rainfall 600-750 mm and annual average temperature 7.0 – 8.5 oC. The investigated soils were forest and meadow cambisols and leptosols. Two samples were collected from each of the eight profiles (the A and the parent rock horizons) to determine the possible variation in the composition of clay minerals within the profile.

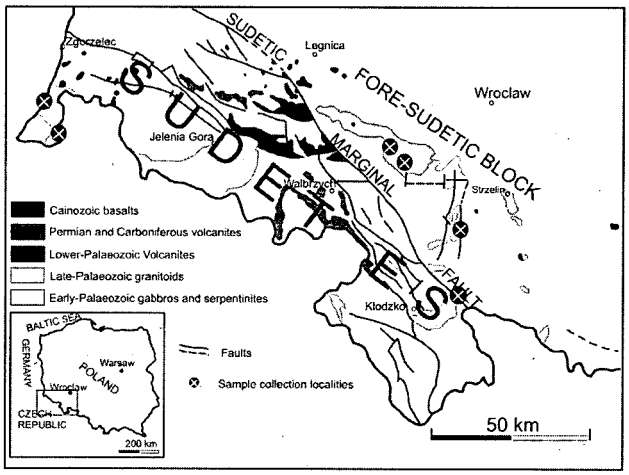

Fig. 1: Sitemap with location of sampling (based on Przybylski [1]).

The study of clay minerals showed that colloidal fraction of soil material – although developed from different granitoids and build up of different feldspars as well as different amounts of mafic minerals – consists of the same minerals. Illite, kaolinite and vermiculite are present in all of the examined profiles, but illite distinctly dominates in soils derived from leucogranite, granite and granodiorite, whereas vermiculite is the main clay mineral in tonalite derived soils, independently of the depth of the soil horizon. On the other hand, soils derived from leucogranite, granite and granodiorite reveal presence of vermiculite in the deeper horizons, while A horizons indicate significant decrease or lack of this mineral. This may suggest the process of transformation of vermiculite into illite, occurring over the time under conditions of temperate climate of Lower Silesia, SW Poland.

There were also differences in clay mineralogical composition between deeper horizons of soils derived from different kinds of granites. Vermiculite was observed in soil material derived from biotite-granite, while there were found only very weak evidence of this mineral in weathered material of two-micas-granite. This confirms that the presence of biotite in rock favours formation of vermiculite during the weathering processes.

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The effect of hydrological conditions and pH on phyllosilicate transformations in pyrite-bearing schist weathering zone in Wieściszowice (Lower Silesia, SW Poland)

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Phyllosilicate transformations in acidic environment were investigated in the area of an abandoned pyrite open-pit mine in Wieściszowice (Lower Silesia, SW Poland) using XRD, FTIR, and SEM-EDS methods. The aim of this study was to determine the influence of hydrological conditions and pH of water on phyllosilicate transformations. Dry (well-drained) as well as wet (waterlogged) saprolite samples were investigated.

Parent rock of well-drained saprolites contained exclusively one kind of phyllosilicate: chlorite or mica. Thanks to this opportunity it was easier to determine a chlorite and mica alteration paths in highly acidic conditions (pH 2–3) separately. The chlorite schist consisted of chlorite, quartz, albite, calcite, and pyrite. Saprolite derived after chlorite schist is composed of sulfate minerals, predominantly slavikite (hydrous Mg and Fe sulfate), which it is probably formed at the expense of dissolved chlorite. Clay fraction of chlorite schist saprolite contained major chlorite and minor amounts of mica which could be redeposited from the higher part of the outcrop. Occurrence of chlorite in saprolite, even though its intense dissolution, may be caused by simultaneous physical weathering of parent rock.

Mica schist mainly consisted of dioctahedral micas: muscovite and paragonite, and quartz as well as minor amounts of albite, chlorite and pyrite. Mineral composition of mica schist saprolite is close to the parent rock with the exception of pyrite which completely weathered. Minor amounts of jarosite were also present. Clay fraction of the saprolite is composed of primary micas as well as secondary smectite, which is main component of fine grain fraction (< 0.2 μm). Presumably, smectite formed mostly at the expense of micas.

Wet samples were collected from extremely acidic Purple Pond (pH 2.7) and less acidic Blue Pond (pH 4.6). Purple Pond water contains large amounts of Fe (135 mg/l), Al (68 mg/l), Si (49 mg/l), and SO_4^{2-} ions (1740 mg/l). Content of these components in Blue Pond is significantly lower. Wet saprolites were evolved from the same parent rock – chlorite-mica schist. It consisted of quartz, albite, chlorite, muscovite, paragonite, and pyrite. Bulk mineral composition of the saprolites is similar to the parent rock, except pyrite, which is removed. Clay fraction of Purple Pond sediment contained large amount of smectite, whereas clay fraction from Blue Pond sample contained interstratified swelling mineral probably composed of smectite and vermiculite layers.

Phyllosilicate alterations in the area of Wieściszowice pyrite mine are stronger in dry conditions than in wet ones. This conclusion can be supported by presence of primary phyllosilicates as major components of clay fraction of wet saprolites as well as low amounts of secondary swelling minerals. In dry saprolites chlorite underwent intense dissolution, whereas dioctahedral micas were transformed into swelling clay mineral, mainly smectite. The pH of water is important factor influencing degree of phyllosilicate transformations in studied waterlogged saprolites. Data obtained during this study suggest that phyllosilicate alterations under the influence of extremely acidic waters of Purple Pond are more advanced than in the Blue Pond. Such feature suggests that the scale of phyllosilicate transformations is directly inversely correlated with pH value.

Mineral composition of the clay fraction in soils with a cambic horizon in the Czech Republic

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Soils with a cambic horizon are commonly found in many regions of Central Europe. Processes leading to the formation of a subsurface cambic horizon are essentially the same in all climatic zones but the intensities of chemical and biological transformations are different. In the Czech Republic extensive research has been done on gneiss [1], granite and gabbrodiorite [2]. This study presents data about the effect of the parent material on mineral composition and basic properties of soils with the cambic horizon.

The research was conducted in agriculturally utilized areas. Soil profiles with a cambic horizon at the localities of Brodce (Cambic Leptosol on calcareous sandstone, 226 m above sea level, 50°20′ N, 14°52′ E), Humpolec (Haplic Cambisol on paragneiss, 523 m a.s.l., 49°33′ N, 15°21′ E), Náměšť nad Oslavou (Haplic Cambisol on paragneiss, 442 m a.s.l., 49°12′ N, 16°09′ E) and Vysoké nad Jizerou (Haplic Cambisol on orthogneiss, 680 m a.s.l., 50°41′ N, 15°23′ E) were selected for this study. Soil horizons and types were classified according to the World Reference Base for Soil Resources [3].

Samples were collected from excavated pits. Main soil properties from individual horizons, such as the particle size distribution, pH values, cation exchange capacity (CEC), organic carbon and nitrogen were analysed using common pedological methods. XRD tests were obtained on a Philips PW 3710 diffractometer. The analysis of the <1 μm fraction was performed on air-dried oriented samples, and then saturated in ethyleneglycol at 80 °C in a furnace for four hours and finally heated to 550 °C for four hours. Semiquantitative analysis was done basing on the areas of individual mineral basal peaks.

The values of pH are predominantly acid. Cambic Leptosol has a weakly acid pH in the upper part of soil profile and a basic pH further down in horizon Ck. The distribution of cation exchange capacity within the profile corresponds with the particle size distribution and content of organic carbon. Cambic Leptosol has a lower value of CEC than Haplic Cambisols.

Organic carbon content and nitrogen are higher in the upper part parts of the soil profiles. The highest values of organic carbon were documented at the localities of Humpolec and Vysoké nad Jizerou. On the other hand, the lowest organic carbon content was obtained at Brodce.

The analysis of the fraction <1 μm showed that the cambic horizon of Haplic Cambisol is dominated – among clay minerals – by illite and also by kaolinite (Humpolec) and by chlorite (Vysoké nad Jizerou). Cambic horizon of Leptic Cambisol has a higher content of kaolinite.

The results revealed differences in the formation of the cambic horizon. A major role is played not only by the parent material but also by other site-specific conditions.

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Characterization of wet clays in TEM

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Characterization of particle size and shape, including surface morphology, is an important step in clay research. Despite previously reported techniques, the precise measurement of clay particle size remains difficult due to the minuscule size and diversity of shapes, surface activities, and sample preparation methods. The key to successful size analysis lies within the ability to keep the particles well dispersed in their natural (wet or specific liquid) environment. This paper presents novel methods and technologies of studying clay minerals in a fully wet (water) environment using different transmission electron microscopy (TEM) techniques.

Special techniques have been developed to overcome the difficulty of clay specimen preparation in their natural state. The wet environmental-cell TEM (WETEM) technique provides a special wet environment chamber at atmospheric pressure in TEM that allows for examination of individual clay particles at high resolution. The cryo-method involved creates a thin vitrified film of suspensions using a specially designed cryo-plunge device. Two spray methods, EFFA spray system and special atomizer, are also applied to disperse clay particles on carbon coated copper grids for TEM observation. Finally, clay nanocomposite samples are dispersed and embedded in epoxy, and ultra-thin sectioned for TEM study.

Large agglomerates with scattered overlapped clay particles are the typical TEM image obtained from conventional specimen preparation techniques. However, with the fore-mentioned techniques, clay particles can be fully or partially dispersed. The wet environmental-cell TEM technique allows *in-situ* observation of individual particles in wet environment, and thus the size and shape of individual clay particles can be analyzed in high resolution. Clay particles of different shapes (e.g., spherical-like, platy, elongated rod-like, needle, triangular, and polygon) of nano-size are observed in WETEM. The fast quench of clay suspensions in Cryo-TEM is capable of preserving different clay orientation before settling occurs. The spray technique using the atomizer offers relatively good dispersion of clay particles whereas the conventional spray system often produces small aggregates.

Experiments utilizing these techniques demonstrate that the fundamental (the thinnest) individual smectitic clay particles appeared to have a very similar measurement of 5 to 10 nm in thickness, with the majority around 5 nm. This thickness is unique and may be universal. Excellent high resolution characterization of clay particles has also recently been achieved by other techniques such as TEM tomography.

Physical interpretation of Scherrer crystallite size for parallel-layered crystallite aggregate

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Scherrer equation was first developed in describing the contribution of the small crystallite size in metallurgy to the peak broadening of X-ray diffraction pattern in the form of full width at half maximum (FWHM) [1], and was hence extensively utilized by chemical physicists, material scientists, applied crystallographers and clay mineralogists to determine the thicknesses of coherently scattering domains (CSD) perpendicular to the diffracting planes for parallel-layer groups of carbon black [1], illite, chlorite [2-6] and other crystallites from the obviously broadened (001) peak profiles. The Scherrer crystallite size thus derived is called "effective length" [7], "apparent crystallite size" [1,7], "effective crystallite size"[3-4], or "realistic mean thickness" [8], etc., and is simply interpreted as CSD mode of thickness distribution [3,5,6], or as mean weighted by number [4,9-11], by area [12,13] or by volume [14,15], when it is compared with TEM-measured crystallite sizes. Here we show by using interference function for one-dimensional X-ray diffraction [9-11,16] that Scherrer crystallite size as frequently used for parallel-layered crystallite aggregate, in particular clay minerals, is actually the mean thickness weighted by number, rather than by area or by volume, and the Scherrer constant is variable, rather than fixed, with the number of layers in each crystallite.

As the interference function depends on the thickness and the thickness distribution of CSDs, an idealized one-dimensional diffraction pattern from perfectly oriented illite or chlorite clay sample was studied and we found by modeling that Scherrer crystallite size is the average thickness weighted by number perpendicular to the diffraction direction c.

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A new approach to the extraction of illite crystal thickness distribution from XRD data

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The classic approach to the calculation of the illite crystal thickness distribution from X-ray diffraction patterns is based on the Bertaut-Warren-Averbach analysis. Before registering the XRD patterns illite and illite-smectite samples are treated with polymer polyvinylpyrrolidone (PVP) in order to split mixed-layer crystals into free fundamental particles. The presence of PVP on the particle surfaces influences XRD patterns. This problem was approximatelly solved by [1].

The alternative approach is based on modeling the structure of PVP on smectite surface and on assumption that the structure of PVP is similar on smectites and on illites [2]. The X-ray diffraction pattern of illite is calculated as a weighted sum of diffraction patterns of illite fundamental particles of particular thicknesses with PVP on their surfaces.

For the purpose of this study a computer program, which employs Genetic Algorithms as the minimization paradigm, was written and tested. It was found that this approach works best if the mean thickness of illite fundamental particles is relatively small.

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Thermal analysis of synthetic hydrotalcite and bauxite refinery hydrotalcites

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Hydrotalcites have the useful ability of removing anionic species from solution either by anion exchange or through the initial formation process of the layered double hydroxide structure. This investigation has looked at removing arsenate and vanadate using hydrotalcites prepared in two different ways: 1) co-precipitation and 2) thermal activation. The thermal activation method has been clearly shown to increase the number of anions removed from solution. This increase in effectiveness is due to the increased chemical reactivity of the hydrotalcite structure after dehydration. Hydrotalcites were prepared using synthetic materials, Bayer liquor, and seawater neutralised bauxite refinery residues.

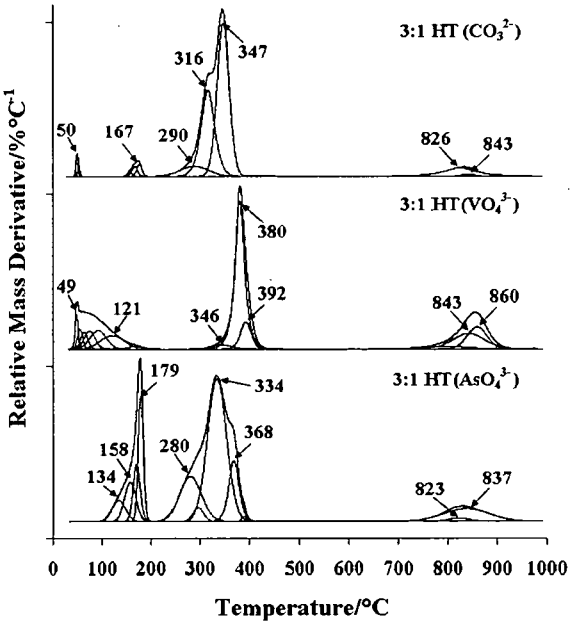

Fig. 1: Thermal analysis patterns of hydrotalcite with intercalated carbonate, vanadate and arsenate.

This work has shown that the intercalation of arsenate and vanadate increases the thermal stability of the hydrotalcite structure compared to carbonate hydrotalcites (Fig. 1). The Mg:Al ratio used for the removal of the toxic anions has been found to be dependent on the method used. For the co-precipitation method the formation of hydrotalcite in solution with a Mg:Al ratio of 3:1 is favoured over the 2:1 and 4:1, whereas for thermally activated hydrotalcites with a Mg:Al ratio of 4:1 is most favourable. Using a variety of techniques the mechanism for the inclusion of arsenate and vanadate has been determined. It has also been established that the removal of toxic anions in highly alkaline solutions is diminished.

This investigation has also shown that Bayer refinery residues may be used for the treatment of solutions containing toxic anions. Thermally activated Bayer hydrotalcite has been shown to be highly effective in the removal of arsenate and vanadate, with 100 % removal being observed. The formation of hydrotalcite during the seawater neutralisation process removes anions via two mechanisms rather than one observed for thermally activated red mud.

Investigation of layered structures using terahertz time-domain spectroscopy

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Model inorganic layered structures based on selected layered minerals from the micas group and boron (aluminium) nitride were investigated in the far infrared region using terahertz time-domain spectroscopy (THz-TDS). This technique allows determination of the complex index of refraction – refractive index and absorption index, including sample thickness determination from single sample and background measurement in the frequency region from 0.1 to ~6.0 THz (3.3 to ~200.0 cm^{-1}). The main advantage for utilization of the THz-TDS is the coherent nature of measured transmitted electric field, providing high sensitivity and resolving phase information [1]. Therefore, this technique is able to deliver frequency dependence of material complex dielectric permittivity related to the refractive properties through Maxwell's relationships.

The samples were characterised also by X-ray diffraction, Fourier transform infrared spectroscopy and other conventional techniques. Micas were selected in such manner that differed significantly in chemical composition e.g. in structural cations and ratios of interlayer cations. For instance the structural iron content as determined by EDS differed significantly. The results of frequency dependent complex index of refraction ($\tilde{n}_s = n_s - i\kappa_s$) of used layered materials were determined.

Acknowledgements: The financial support of the Slovak Grant Agency for Science VEGA grant No. 1/4457/07 and of the Slovak Research and Development Agency APVV grant APVV-0491-07 and grant VMSP-P-0110-09 is greatly appreciated.

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The benefits of the near-infrared spectroscopy in the characterization of organoclays

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Near infrared (NIR) spectroscopy belongs to spectroscopic methods with dynamic development and spreading into many areas of science and technology, however, its utilization in the organoclays studies is rather rare [1-4]. Detailed analysis of the NIR spectra of montmorillonite-based organoclays was performed to show the advantages of this spectral region in their characterization and in identification of specific bonds "not visible" in the middle infrared (MIR) region. Na-saturated <2 μm fraction of bentonite from Jelšový Potok (Slovakia) was used for organomontmorillonites preparation. Different alkylammonium cations were selected to allow more ways of comparisons of the spectral features within the series. Four samples contained various amounts of octylammonium chains: monooctyl- (1C8), dioctyl- (2C8), trioctyl- (3C8), and tetraoctyl- (4C8) ammonium, while two others had chains of double length, hexadecyl- (1C16) and dihexadecyldimethyl- (2C16) ammonium. Last two cations were of different structure containing aromatic benzene, either without double bonds benzyltrimethylammonium (C10) or with a reactive double bond present in 4-vinylbenzyl-trimethylammonium (C12).

Similar shape of the MIR patterns of CH_3 and CH_2 stretching (3000-2800 cm^{-1}) and bending (1500-1300 cm^{-1}) vibrations was observed within 1C8-4C8 and 1C16-2C16 series. However, the spectra of the samples with 16 C atoms - 2C8 and 1C16, and 32 C atoms - 4C8 and 2C16, were significantly different due to altered ratios of CH_3 and CH_2 groups in the cations. Only weak bands corresponding to stretching NH_3^+ and NH_2^+ vibrations (~3270-3190 cm^{-1}) were resolved in the MIR spectra of 2C8, 3C8 and 1C16, the NH^+ band was overlapped with the CH and/or H_2O vibrations. Only vibrations of trimethylammonium cations were clearly identified in the MIR spectra of C10 and C12, weak bands near 3100 cm^{-1} should correspond to Ar-CH (Ar = aryl). Vibrational modes of Ar-C-C, or H_2C=C (vinyl) group were overlapped with more intense vibrations of aliphatic CH groups.

Based on the vibrations observed in the MIR region the first overtone ($2\nu_{XH}$) and combination $(\nu+\delta)_{XH}$ bands of XH groups (X = O, C, N) were identified in the NIR spectra of organo-montmorillonites. The complex band near 7070 cm^{-1} was assigned to overlapping $2\nu_{OH}$ of the structural OH groups and bound H_2O molecules, the combination modes of H_2O and structural OH groups were found near 5250 cm^{-1} and 4523 cm^{-1} respectively. The intensity and the position of the $(\nu+\delta)_{H2O}$ band was strongly affected by the type of the organic cation used. While the presence of CH_3 and CH_2 groups in 1C8-4C8 and 1C16-2C16 samples was recognized in the 6000-5500 cm^{-1} ($2\nu_{CH}$) and 4450-4100 cm^{-1} $(\nu+\delta)_{CH}$ regions, the overtone and combination bands of Ar-CH (C10 and C12 sample) were clearly shifted to higher wavenumbers. The NIR spectra were found to be extremely useful to identify NH and vinyl groups, which were difficult to recognize in the MIR region. The intensive bands of the first overtone and combination modes of NH_3^+ and NH_2^+ were found in the 6600-6050 cm^{-1} and 5000-4600 cm^{-1} regions, respectively. Though no NH^+ overtone was observed in the NIR spectrum of 3C8, the intensity of the $(\nu+\delta)_{NH+}$ near 4750 cm^{-1} was high enough to unambiguously identify this bond. The characteristic band assigned to $2\nu_{CH2}$ in H_2C=C at 6130 cm^{-1} was detected in the spectrum of C12.

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FTIR and UV-Vis spectroscopic investigation of illite-smectite minerals from Dolná Ves (Slovakia)

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Information available from the most common spectroscopies, infrared and UV-Vis, on illite-smectite (I-S) mixed layer minerals is discussed. Figure 1 shows the IR spectra of samples containing a montmorillonite (JP, Jelšový Potok, Slovakia), an I-S (DVS, Dolná Ves, Slovakia) and an illite (Mo, Morris, Illinois, USA). XRD analyses prove 30 and 9 % of swelling interlayers, respectively, in I-S and illite [1]. The IR spectra of JP and DVS suggest similar chemical composition with AlMgOH bending vibrations near 845 cm^{-1}. Higher Al^{IV} for Si substitution in illitic layers generates the Al^{IV}-O (~830 cm^{-1}) and Al^{IV}-O-Si (755 cm^{-1}) vibrations.

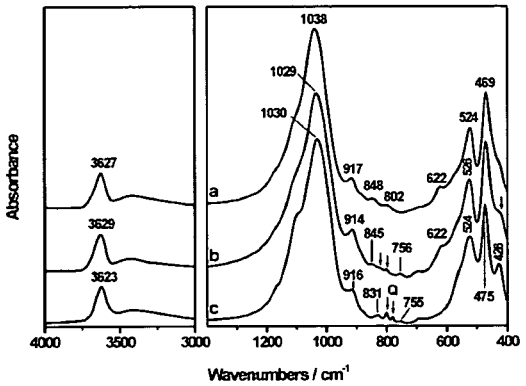

Fig. 1: IR spectra of < 2 μm fractions of a) JP montmorillonite, b) DVS illite-smectite and c) Mo illite; (Q = quartz).

The presence of illitic layers in DVS and Mo modifies the shape of the IR pattern near 620 and 420 cm^{-1}. The well developed band at 622 cm^{-1} in the JP spectrum corresponds to coupled Al^{VI}-O and Si-O vibrations. The intensity of this band is lower for DVS and it is absent from the Mo spectrum. The reverse sequence is found for the Si-O band at 428 cm^{-1}. A well developed band appears for Mo, a shoulder for DVS, and no absorption for JP. A similar dependence was found for a set of DVS samples with different expendability. These IR features may help to differentiate illitic layers in clay samples but not to distinguish between a mixture of individual minerals and an I-S.

Cationic dyes, such as methylene blue or Rhodamine 6G (R6G), form molecular aggregates on clay surface and change their colour. Dye cation agglomeration is a good tool for testing layer charge density on smectites which affects the distance between the dye species. Formation of aggregates results in creation of different forms of the dye, absorbing visible light at different wavelengths. Second-derivative of UV-Vis spectra (SDS) of a series of I-S from DVS deposit with R6G show a direct relationship between the SDS amplitude for the band assigned to the H-aggregates and the expandability. I-S interact with R6G more intensely than do smectites [2].

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Structure elucidation of organoclay-polymer composites by instrumental techniques

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The industrial application of layer-structured minerals depends on their surface reactivity. In addition to the common applications (e.g. paper, plastics, rubber, pharmaceutical and ceramic industries) they can improve the physical and/or chemical properties of polymers as additives in an amount of 2-5 %. The requested properties can be achieved by the addition of highly dispersed (micro- or nanoscaled) minerals (kaolinite, halloysite and montmorillonite) embedded in the polymer (e.g. polypropylene, polyethylene and polycaprolactone) matrix. The use of reactive modifiers is also necessary to ensure compatibility between the mineral particles and the polymer.

Organoclay nanocomposites can be obtained either by ion exchange (in the case of montmorillonites) or by intercalation (in the case of halloysites and kaolinites in solution or with mechanochemical treatment). Since property improvement is proportional with increased dispersity and reduced particle size of the mineral additive, delamination and the formation of nanotubes is the main goal of this research. The structure of the nanocomplexes formed and that of the clay-polymer composites prepared can be investigated by instrumental techniques such as FTIR (DRIFT) spectroscopy, Raman microscopy, thermal analysis combined with mass spectroscopy, XRD, etc.

Delamination of different kaolinites and halloysites was made by multiple intercalation using urea and triethanol amine. With an electrophilic agent tetraalkyl ammonium cations have been synthetized between the layers reacting with a polyacryl sodium salt added to the system.

Polymer nanocomposites have been prepared by melt mixing in a twin-screw extruder at temperatures of 130 (PCL), 200 (PP) and 250°C (PA).

The addition of 1,3-phenylenedimaleimide (BMI) as reactive modifier further increased the expansion of montmorillonite and improved all of the end-use properties of the polymer. The most significant effect (some 80%) was the improvement in gas permeability. Dissimilarly to montmorillonite-based nanocomposites, no further expansion was observed with 1:1 type minerals with the addition of BMI. In this case improvement in mechanical properties was due to BMI forming an interphase between the clay particles and the polymer matrix.

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The effect of dry grinding on the structure of sepiolite from Turkey

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The effects of grinding on clay minerals are investigated with great interest because this process produces changes in the textural and structural properties of powdered material.

Sepiolite is a fibrous hydrated magnesium silicate and a natural clay with a unit cell formula $(Si_{12})(Mg_8)(O_{30})(OH)_4(OH)_2 \cdot 8H_2O$ [1]. This mineral is 2:1 layer silicate, which means that the octahedral layer is bound above and below by a silica tetrahedral sheet. The tetrahedral sheets are linked infinitely in two dimensions. It is structurally different from other clay minerals in that the octahedral sheets extend in only one dimension and the tetrahedral sheets are divided into ribbons by a periodic inversion of rows of tetrahedrons [2].

The sepiolite powder sample supplied from Element Mining Co., Eskişehir. The raw mineral was subjected to dry grinding by ball milling, for periods ranging from 0 (smaller than 40 μm) to 120 min, using a planetary ball mill (Fritsch Pulverisette 6).

The physico-chemical and structural alterations are determined by particle size distribution (PSD), specific surface area (BET method), density, porosity, color (L, a, b), X-ray diffraction (XRD), scanning electron microscopy (SEM), FT-IR analyses were carried out. According to the mineralogical and chemical analysis results, the raw mineral can be accepted pure sepiolite ore (Table 1). With grinding, the rate of size reduction decreases with time, but reduction continues up to about 30 min. At this time of grinding, particle size reduction decreases with time, but reduction continues up to about 30 min. Grinding of sepiolite produces an increase of the starting BET surface area value progressively up to a maximum of 364 m^2g^{-1} at 30 min. A subsequent decrease of surface area with increasing grinding time was observed. A breakdown of the initial particles due to grinding effect observed more rounded particles, aggregates and agglomerates, as proved SEM images.

Table 1. Chemical, mineralogical composition and some physical properties sepiolite

Chemical analysis	Unit	Value
SiO_2	wt%	51.76
MgO	wt%	21.42
CaO	wt%	0.73
Al_2O_3	wt%	4.43
Fe_2O_3	wt%	1.83
K_2O	wt%	0.46
Na_2O	wt%	0.13
TiO_2	wt%	0.24
MnO	wt%	0.09
LOI*	wt%	18.9
Total	wt%	**99.99**
Mineralogical analysis		
Sepiolite	wt%	%85.7
Dolomite	wt%	10.4
Quartz	wt%	3.9
Physical Properties		
Density	g/cc	2.34
Specific surface area	m^2/g	265.12

*LOI: Loss on ignition

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AFM study of vermiculite particles

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Atomic force microscopy (AFM) has been evolved as a promising device to explore the mineral surface, determine morphology, visualize the sorption of organic substances, measure size and thickness of clay-size particles and also measure growth, dissolution, heterogenous nucleation and redox processes [1]. AFM is a powerful technique for the characterization of particles with the size ranging from 1 nm to 10 μm and therefore it can be used for exploration of clay minerals [2,3].

Vermiculite small particles were prepared using two milling procedures. Each sample was milled for 15 minutes in jet mill (Sturtevant Micronizer®) parallel with 15 min of milling in planetary ball mill (wolfram carbide mill chamber and balls). Jet milling was realized with the pressure of compressed air (as the grinding energy) 350 kPa and constant feed rate of grinding material (1.5 g/min) to obtain particles of size approximately 2 μm. Both vermiculite powder fractions showed uniform mean particles size of 3 μm, as it was determined using the laser method (Fritsch Particle Sizer Analysette 22). Morphology of vermiculite particles was examined using the scanning electron microscope (SEM).

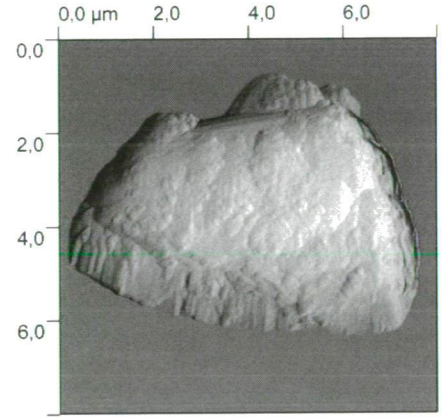

Fig. 1: The 2D AFM image of jet milled vermiculite particle.

In comparison to the traditional technique (SEM), AFM can give 3D and 2D images with Z information through color intensity, providing the opportunity to obtain quantitative measurements of particles using GWYDDION software.

The morphology of the milled vermiculite particles was studied with atomic force microscopy AFM-Explorer™. The suspension of the vermiculite powder in anhydrous ethanol was placed on mica plate and then dried at 60°C for 10 minutes. The AFM scanning was performed with the silicon probe 1650-00 in non-contact mode with 8 μm Z-linearized dry scanner.

The particle size distribution, orientation and the aspect ratio of vermiculite particles after different mechanical disintegration procedures were by the help of AFM with non-contact mode successfully studied.

Acknowledgements: This work was supported by the Grant Agency of Czech Republic GAČR grant no: 205/09/0352.

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Gas barrier properties of natural rubber/mechanochemical treatment coal bearing strata kaolinite nanocomposites prepared by melt blending

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Nanocomposites materials are two-phase systems that consist of a polymeric matrix and dispersed inorganic particles of nanometer scale [1]. The use of organic clays as precursors to nanocomposite formation have been extended into various polymer systems including epoxys, polyurethanes, nitrile rubber, styrene-butadiene rubber, isobutylene–isoprene rubber and ethylene propylene diene monomer [2,3]. Kaolinite-rich rocks are very abundant in the Permo-Carboniferous coal-bearing strata of North China and are widely used [4]. Thereafter, coal bearing strata has been applied to incorporate the layered silicates in polymer hosts by in situ polymerization, solution intercalation or simple melt mixing. Recently, much of the work clay application in the rubber has been done to improve the barrier performance of rubbery materials with organic montmorillonite particles [5], and there are relatively few reports on organic kaolinite in this application.

The X-ray diffraction pattern at room temperature indicated that the intercalation of potassium acetate into kaolinite causes an increase of the basal spacing from 0.718 to 1.42 nm, and with the particle size reduction, the surface area increased sharply with the intercalation and exfoliation by ball-milling. the particulates have high aspect ratio according SEM images.

It is also shown coal bearing strata kaolinite layers are finely dispersed into the natural rubber matrix and orientationally arranged in parallel. These highly filled natural rubber/mechanochemical coal bearing strata kaolinite (NR/MCBK) nanocomposites exhibit outstanding mechanical properties, excellent gas barrier properties and much higher thermal stability compared to the pure natural rubber. The significant improvements in the mechanical properties (Table1), thermal stability and gas barrier properties may be attributed to the restriction of the parallel kaolinite platelets to the free movement of rubber molecule chains and the retardation of the impermeable kaolinite layers to the progress of gas molecules through the rubber composites.

Table 1: Mechanical properties of NR composites filled with various MCBK loadings

MCBK content /phr	Hardness (HA)	Stress /MPa		Tensile strength /MPa	Elongation at break /%	Permanent set /%
		300%	500%			
0	37	1.89	5.49	23.2	745	25
70	55	4.35	14.2	25.2	663	68

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Thermal analysis of China kaolin –kaolinite, coal-bearing strata kaolinite and halloysite

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Kaolinite and its polytype, halloysite have a wide variety of applications in industry [1]. These applications include their use in the fabrication of paper, paints and inks, rubber and plastic, ceramic raw material, medicines, etc. [2-4]. Most of the industrial kaolin in china which generally contain a certain amount of organic carbon need to be calcined to improve whiteness [5]. Thermal stability and whiteness are very important properties of calcined kaolin particularly for industrial applications [6]. Therefore, the thermal analysis of kaolin also gives new insights not only about improvement of the properties but also protection of the environment.

Comparing the temperature of dehydroxyl, it is established that kaolinite with lower Hinckley crystallinity index dehydroxylates easilier than those whoes Hincley index are high. The comparison of kaolinite and hallosite is shown that the thermal decomposition of kaolin is determined by different factors, such as degree of the structural ordering, mineral impurities and adsorbed and substituted ions. The mass gain in the MS curves corresponds precisely with the mass loss in the TG curves.

The thermal decomposition of kaolin occurs in main three main steps (a) desorption of water blow 100 °C, (b) dehydration at about 225°C, (c) well defined dehydroxylation at around 450°C (Fig. 1).

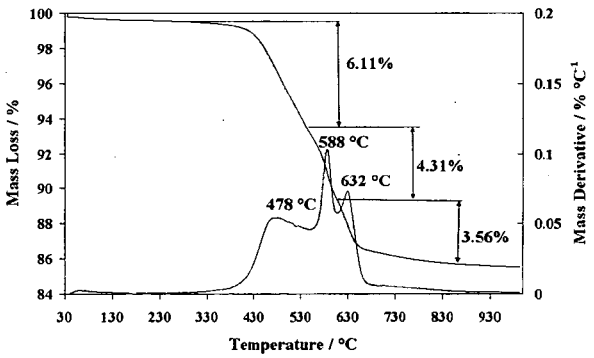

Fig. 1: TG and DTG curves of coal bearing strata kaolinite.

The temperature of dehydroxylation of kaolinite is found to be influenced by the degree of disorder of the kaolinite structure and the gases evolved in the decomposition process can be various because of the different amount and kind of impurities. It is evident by the mass spectra that the interlayer carbonate from impurity of calcite is released as CO_2 around 225, 350 and 710°C in the kaolin samples. TGA-MS show the coal bearing kaolinite released CO_2 about 450°C. Thus for geosequestration decarbonization and purification before industry application of kaolin is necessary.

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Characterization of bleaching phenomena in German red bed sediments by directly coupled evolved gas analysis (DEGAS).

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In this study varied coloured Buntsandstein sandstones in Central Germany (Thuringian Vorderrhön) were investigated by a thermo-gravimetric/pyrolytic method (DEGAS – directly coupled evolved gas analysis) to analyse the degassing behaviour of red bed sediments and their bleached modifications. Often such bleaching of primary red bed sandstones is contributed to fluid-rock interactions. Therefore the investigations were focused on geochemical/mineralogical features of such sediments to validate the causes of such bleaching processes. The pyrolytic experiments were performed using a commercial, slightly modified NETZSCH TG-MS system (thermobalance coupled directly to quadrupole mass spectro meter). All gaseous species were analysed in multiple ion detection mode and correlated with the total pressure change in the sample chamber during heating (temperature range: from room temperature (22°C) to 1200°C and 1450°C, respectively) [1]. The ion current for different mass/charge ratios (e.g. m/z 18, 44 & 78, Tab. 1) was recorded as a function of time. Depending on the amount of volatiles in the sample about 10 mg of sample material were used. The samples were taken from core plugs and carefully prepared without using cooling additives to avoid any contamination.

Table 1: Detected element species during MS analysis

Mass number	Fragment ions	Geogene source
1	H^+	sheet silicates,
2	H_2^+, D^+	hydroxides,
17	OH^+, NH_3^+	hydrates
18	H_2O^+	& organic material
28	N_2^+, $C_2H_4^+$, CO^+	carbonates
44	CO_2^+, $C_3H_8^+$, N_2O^+	& organic material
78	$C_6H_6^+$	organic material

Degassing patterns of sample M44 indicate a preferential breakdown of sheet silicates, hydroxides, hydrates and carbonates [2]. Its two red subsamples M44-R1 and -R2 are dominated by the release of H_2O and CO_2, whereas in the two bleached subsamples M44-B1 and -B2 an additionally H^+ source without any correlation with m/z 17 and 18 occurred, probably due to the presence of hydrocarbon species. Another Buntsandstein sample M49 was separated into 12 subsamples representing a profile from unbleached to bleached rock portions. The increase of m/z 44 in subsamples M49-1, -3 and -9 are attributed to small carbonate domains in the sample. A prominent signal of m/z 78 in the transition zone between bleached and unbleached areas implies the presence of a further hydrocarbon species.

The performed mass spectrometric gas analysis sustain geochemical differences in red and bleached sandstone rock composition, sometimes only weakly maintained by conventional geochemical methods (XRF, ICP). The results constrain that DEGAS might serve as an efficient and complementary analytical tool in sedimentary research in evaluating the involvement of specific gaseous species during fluid-rock processes.

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X-Ray Diffraction and lithologico-mineralogical studying of Kazakhstan clay minerals

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Among all existing methods of studying the mineral structure of clay minerals, the X-Ray method is the most authentic. More over, the X-Ray method can state a quantitative estimation whereas other methods are qualitative. From X-Ray methods it is most effective diffractometrical.

In the present work, roentgenograms of clay minerals have been obtained on X-Ray Diffraction type DRON – 3 with CuK_α – radiation, monochromatized by graphite monochroma-tor installed in the front of the counter. Interpretation of diffractograms has been carried out with the help of the ASTM Powder diffraction card file datas and diffractograms purefied from impurities of minerals. The Kazakhstan samples of clays Taukentsky, Akkalkinsky (2 samples) and Akzharsky deposits have been investigated.

Results of X-ray and also lithologico – mineralogical analyses have shown that Taukentsky clay concerns clays of hydromicas-mont-morillonite group with prevalence of montmorillonite component of alkaline-earth calcium–magnesian form. In the investigated sample crystallites of blended-layer formations are formed which decrease exchange capacity of a clay. Estimated content of a hydromicaceous component is 10–15 % and montmorillonite component – 60 – 65 %. The total content of a clay component is approximately 80 %.

An assay of Akkalkinsky clay (the sample № 1) consists of 79.4 % of pelite fractions (<0.01 mm); 15.8 % of aleurite fractions (0.01–0.1 mm); 4.8 % of sandy fraction (> 0,1мм). The sample № 2 of Akkalkinsky clay consists of 91. 0 % pelite fractions, 8.8 % aleurite fractions and 0.2 % – sandy. By the prevalence of montmorillonite clay (both samples) concerns to bentonite type.

By the results of the mineralogical analysis Akzharsky clay concerns to adjournment bottom Eocene and is combined bentonite clays of is light – grey to dark – grey colour, fat, high-plastic, as soap with the raised maintenances montmorillonite. On the figure diffractogram of Akzharsky clay is shown.

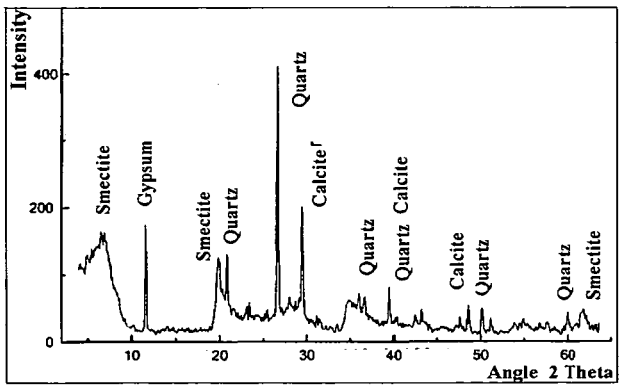

Fig. 1: Diffractogram of Akzharsky clay.

Thus, X-Ray diffraction and lithologo-mineralogical studying of clay minerals of the Kazakhstan deposits has allowed to draw a conclusion that montmorillonite component of the studied minerals allow successfully use them as raw materials for preparation drilling muds in geology-prospecting and oil-gas industries.

Study of dispersions and thin films based on montmorillonite and fluorescent dyes

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Preparation of novel organic-inorganic nanocomposites reflects their significant potential for its possible utilization as novel materials e.g. shown in the recent years in combinations with polymers and semiconducting polymers [1] with electroluminiscent properties. These nanocomposites are forward-looking not only for improved mechanical properties, but in the case of luminiscent materials, they could also provide broadening of spectral field compared with conventional semiconductors. Properties of these nanocomposites are dependent not only on the properties of individual components, but also on their morphological properties, the character of the phase interface, charge characteristics of clay lamellas, etc.

In our study we are trying to shed more light on the preparation conditions of the fluorescent dyes based nanocomposites, while the functional skeleton is based on the organized structure of the sodium montmorillonite particles. The sense of its preparation rests on the fact that this material may be used as narrow frequency response on the exciting radiation, polarisation component in optical devices, or as a part of the solar panels or devices, where the energy transfer with high effectiveness is necessary.

In most studies related to the nanocomposite materials preparation based on clay minerals with negative layer charge and organic cation molecules, the production of the aggregates of organic molecules [2] occurs on the surface of clay mineral. The disadvantage of the production of the aggregates is that their optical and other properties are different from the properties of their monomer form. In the report related to this issue, we assume that the arised problem can be solved by additing the appropriate spacer (β-cyclodextrin), which is able to interact with one organic molecule for purpose of the supramolecular complex formation. The outcome is that we suppose the prevention of the molecular aggregates creation.

Acknowledgements: This work was financially supported by grants from Slovak Ministry of Education VEGA 1/4457/07, Comenius University UK/143/2009 and APVV-0491-07.

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Preparation of nano-spherical smectite particles by hybrid atomization

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Nano-particles of smectites have various applications related to catalysis, catalytic support, adsorption and development of new functional nanomaterials. We present a novel process called hybrid atomization in the production of nano-spherical particles of smectites. Hybrid atomization is new technique that combines gas atomization with centrifugal atomization [1,2]. Such process has been successfully applied in the production of fine, spherical metal powders at lower costs. The average sizes of the powders are 20 μm in diameter with a homogenous size distribution.

In its use for molten metals, the melt is broken into several tens to several hundreds μm droplets by gas atomization and subsequently sprayed on a high speed rotating disk. A thin film of liquid less than 10μm is formed on the disk and the fine droplets are scattered from the edge of the disk. For the case of aqueous suspensions and organic solvents, the atomization modes can be used to control a homogenous size distribution and a desired shape for nano-particles of smectites. The products were characterized by XRD, SEM and TEM. The results will be compared further with those from conventional methods such as spin-coating and spray-dry methods.

These results confirmed that the nano-spherical particles with narrow size distribution from smectites were formed following the same atomization mode, that is, ligament formation in the case of the aqueous solutions and organic solvent. A new process, hybrid atomization method, would effectively produce the inorganic nano-spherical particle for any chemical compositional system.

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Short Wavelength InfraRed petrology: a new laboratory and remote sensing method in low to very low-grade pelites

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Since Kübler (1967) [1], X-ray diffraction has become a standard method to characterize the metamorphic grade of metapelites metamorphosed under very low- and low temperature conditions. This method is based on the full width measurement of the first illite/muscovite peak at middle height (FWHM).

The few attempts that have been made to quantitatively apply spectroscopy methods to K-white mica in the field of very low-grade petrology focused on the infrared wavelength area ('Flehmig index' [2]) and have gained little application [3].

The new illite spectral maturity (ISM) method uses Short Wavelength InfraRed Reflectance spectroscopy (SWIR) to measure K-white mica mineral physicochemistry within very low grade metamorphic pelites. The three ISM measures used in this study parameterize the absorption features at 1900 nm and 2200 nm in terms of their area, depth and asymmetry. Through comparison with the powder XRD-derived Kübler index it is demonstrated that ISM allows the differentiation of anchizonal from diagenetic domains in very low-grade pelites (Fig. 1).

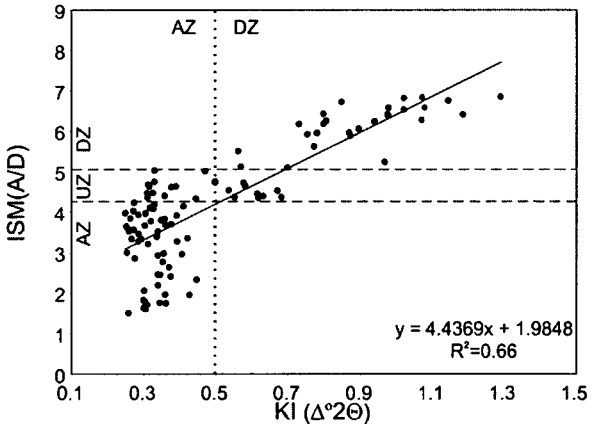

Fig. 1: Correlation between KI (in Δ°2Θ) and ISM measures determined by SWIR. The black dotted line corresponds to the anchizone/diagenetic zone boundary after Kisch et al. (2004), and the stippled lines define the 'unassignable zone' (UZ) for the ISM measures based on that boundary. AZ – anchizone; DZ – diagenetic zone.

The wavelength of the 2200 nm absorption feature provides a measure of the celadonite substitution. It shows a linear correlation (R^2=0.85) with K-white mica *b* cell dimension (powder XRD), and can be used to differentiate the metamorphic pressure facies and related geothermal gradients in pelites of greenschist facies and anchizonal metamorphic grade. The boundaries between LP/MP and MP/HP facies series can be defined at 2204 and 2220 nm, respectively.

[1] Kübler, B. (1967) in Schaer, J.P. (ed.) *Étages tectoniques*. Colloque de Neuchâtel 1966, 105-122. [2] Flehmig, W. (1973) *Neues Jb. Miner. Monat.*, **7/8**, 351-361. [3] Hunziker, J.C. et al. (1986) *Contrib. Mineral. Petrol.*, **92**, 157-180.

Quantification and identification of illite/smectite interstratifications at nanometric scale: association of TEM/EDS/SAED

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In the context of CO_2 sequestration, studies aimed at characterizing the sealing capacity of the argillaceous barriers and at constraining their evolution. In that case, clayey cap-rocks play a key role on confining function supported by their petrophysical properties. The illites-smectites are one of the main components of the CO_2 storage cap-rock in the studied area, the Paris basin. A study [1] points out an illitization of the initial matrix upon micrometric reactive fronts when samples are subjected to supercritical CO_2 in laboratory conditions (with mix of CO_2/H_2O from pure water to pure CO_2). For a good enough safety assessment, the numerical modellings must take into account the geochemical interactions at the reaction's scale: identification of initial/new crystallized minerals and their evolution along the I:S ratio. Such characterizations can be performed by a few precise and routinely practical methods [2]. The technical difficulties of characterization are related to the clays crystals small size and their apparent chemical composition heterogeneity due to the deposition and burial history through diagenesis transformations. A method has been developed that combine both crystallographic data obtained from selected area electron diffraction (SAED) and chemical analyses obtained by energy dispersive spectrometry (EDS) using a transmission electron microscope (TEM). This association allows to determine the ratio I:S and their chemical composition at nanometric scale of the same I/S crystal. Natural references and synthetic I/S, which have been characterized by X-Ray Diffraction (XRD) are used to test the method. The natural I/S are constitued of both ISCz-1 which is a Clay Mineral Society standard and samples from Saint Martin de Bossenay (Paris Basin, France). The synthetic I/S result from an illitization process of synthetic smectites. The advantage of these synthetic materials is the strict control of the chemical composition and the mixed-layering level. The results of SAED patterns along c* obtained from specific preparation (resin exchange, preferential orientation, ultrathin cut) allow the discrimination between illite, smectite and illite/smectite. The chemical analyses confirm an illitization process and ratios.

[1] Kohler, E. et al. (2009) *Clay. Clay Miner.*, **57**, 616-637. [2] Murakami, T. et al. (2005) *Clay. Clay Miner.*, **53**, 440-451.

Comparison of approaches for modelling disorder of clay structures in Rietveld phase analysis

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The complicated and variable disorder of the common clay minerals hampers the adequate modelling of the diffraction profiles as necessary for correct structure and phase analysis by the Rietveld method. Various types of stacking faults occur solely and mixed in natural layer silicates, e.g. well-defined translations and rotations of adjacent identical layers, turbostratic stacking, and mixed-layering of different layer types. Consequently, a number of approaches have been introduced to fit the experimental diffraction patterns. Typically, the anisotropic line broadening by well-defined stacking faults is described by any *hkl*-dependent line broadening model, e.g. [1,2], based on an ideal mean structure. Turbostratic disorder can be approximated by the single-layer approach [3]. Mixed-layering may be modelled by introducing the recursive calculation [4] in a supercell structure model [5]. However, in practice the true type of disorder may be unknown, or a complex disorder model in recursive description needs overmuch computing time for routine purposes. In such cases, an empirical approximation based on manually modified *hkl*-lists [6] may be useful. Such *hkl*-lists can be used together with all other types of structural models.

The presentation discusses the advantages and limitations of the different approaches, focusing on their application in quantitative phase analysis using the Rietveld method. The problem is demonstrated for 1:1 and 2:1 dioctahedral minerals with different types of disorder (pure phases and mixtures). Typically, *hkl*-dependent line broadening models can be applied just to a certain degree of disorder, but may fail when applied to minor components. Flexible but complicated models tend to yield overestimation of phase abundances in mixtures if phases with similar structures are present. Recursive calculation may approximate real patterns very well, but even an extensive fixing and constraining of parameters does not always prohibit tedious computation time. The application of *hkl*-lists [6] may help to speed up routine work to obtain reliable mineral quantification, but does not allow structural investigations of those phases described with the proposed *hkl*-lists.

[1] Bergmann, J. & Kleeberg, R. (1998) *Mat. Sci. Forum*, **278-281(1)**, 300-305. [2] Popa, N.C. (1998) *J. Appl. Cryst.*, **31**, 176-180. [3] Ufer, K. et al. (2004) *Z. Kristallogr.*, **219**, 519-527. [4] Treacy, M.M.J., Newsam, J.M. & Deem, M.W. (1991) *Proc. R. Soc. London*, **A433**, 499-520. [5] Ufer, K. et al. (2008) *Z. Kristallogr. Suppl.*, **27**, 151-158. [6] Taylor, J.C. & Matulis, C.E. (1994) *Powder Diffr.*, **9**, 119-123.

Globular layer silicates of the illite-glauconite series, the Upper Proterozoic, northern Siberia, Russia

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A representative collection of globular dioctahedral 2:1 layer silicates from marine deposits (predominantly silicoclastic, rarely, glauconitites, limestones, dolomites, clayey rocks) of the Lower and Middle Riphean (Osorchayata and Arymass, Debengda, Khaipakh Formation, respectively) and the Vendian (Maastakh Formation) of the Olenek Uplift and of the Lower (Ust'-Il'ya Formation) and the Lower-Middle Riphean (Ysmastakh Formation) of the Anabar Uplift (Northern Siberia, Russia) has been studied. The mineralogical studies were performed by a complex of modern chemical and physical methods (X-ray diffraction, oblique-texture electron diffraction, scanning electron microscopy, classical chemical and micro-probe analyses, Mössbauer spectroscopy etc.), which allowed determining structural and crystal-chemical varieties of the minerals. Best-preserved grains were used for isotope dating.

The glauconite grains have globular, irregular and platy shapes. In the diagenesis zone glauconite globules seem to have been formed by synthesis from colloidal solution, and platy glauconite, by transformation of terrigenous Fe-mica (biotite). Glauconite was mainly formed with the active influence of microorganisms.

Among the studied layer silicates continuous series of solid solutions from illite ($^{VI}Al/^{VI}Al+ {}^{VI}Fe^{3+} \geq 0.6$) via Al-glauconite (Fe-illite) to glauconite ($^{VI}Al/^{VI}Al+ {}^{VI}Fe^{3+} \leq 0.5$) has been observed. Some samples consist entirely or partly of proper glauconite of the Middle Riphean (Debengda Formation) and the Lower Riphean (Ust'-Il'ya Formation). Illite (rarely, Al-glauconite) have been revealed in the Lower and Middle Riphean (Osorchayata and Arymass, Debengda, Khaipakh, respectively) and the Vendian (Maastakh Formation).

Structural varieties from mica to mixed-layer phyllosilicates (≤10 and >10% smectite layers respectively) have been determined. Mixed-layer silicates with a trend to ordering in the alternation of mica and smectite layers (short-range order factor S>1) have been found in Debengda and Khaipakh Formations. The transition from Al-species to Fe-species is accompanied by a variation of the unit cell *b* parameter from 9.00 to 9.08Å.

Mg-rich Al-glauconite has been found in dolomites of the Ysmastakh Formation. This mineral is characterized by unique structural and crystal-chemical peculiarities caused by non-equilibium conditions in reduction zone of shallow dolomite deposits.

Among the studied samples there are globules consisting of two mica (glauconite, illite) phases (Ust'-Il'ya Formation) (b=9.00–9.08Å). The compositional division in biphase globules occurred at the level of individual microcrystals (0.5–5μm) of micaceous minerals. These minerals form an isomorphic series from Al to Fe-varieties within a single globule.

The studied rocks containing globular glauconite-illite minerals are altered by deep diagenesis. Globular and platy grains of illite (Osorchayata Formation) show the same rejuvenated ages. The isotopic ages of globular glauconite-illite minerals of other studied formations correspond to their stratigraphic positions.

Deposition of layered double hydroxides on alumina support

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Layered double hydroxides (LDHs) are often used as precursors for preparation of mixed oxide catalysts. A deposition of LDHs on supports would be advantageous due to a better utilization of usually expensive active components. In this work, a formation of LDHs on anodized aluminum foil is studied; the hydrothermal reaction in aqueous solutions containing divalent metal nitrates [1,2] was adopted to obtain supported LDH and mixed oxide layers. The composition and molar ratios of metal cations in used solutions were adjusted as follows: Ni-Mn (2:1), Co-Mn (2:1), Ni-Co-Mn, Ni-Cu-Mn and Co-Cu-Mn (all 1:1:1); total metal ion concentration of 0.1 mol l^{-1} and pH of 6.8 and 8.5 were applied and the deposition was carried out under hydrothermal conditions at 140°C for 65 h.

Powder XRD patterns of the samples obtained after hydrothermal reaction showed well-crystallized hydrotalcite-like phases. A formation of M^{II}-Al and M^{II}-Cu-Al LDHs (M^{II} = Ni and/or Co) with only a slight Mn content can be expected. An increasing pH in the solutions enhanced the LDH deposition and facilitated incorporation of Co and Mn in the solid; on the other hand, products with lower Cu content were obtained. It can be explained by a difference in the pH, at which various divalent metal hydroxides are precipitated. The products obtained at higher pH showed an increased lattice parameter *a*; it also indicates a higher concentration of Mn cations in the formed LDHs.

Relatively homogeneous layers consisting of thin curved platelets oriented nearly perpendicularly to the support were observed in SEM images. The same morphology of the deposited products was found also in the samples calcined at 500°C (Fig. 1). NiO-like and spinel-like mixed oxides were formed during calcination of Ni- and Co-containing samples, respectively, but no distinct Cu-containing phases were detected by XRD in the obtained M^{II}-Cu-(Mn)-Al oxides. The LDH-related mixed oxides deposited on Al_2O_3/Al support exhibited a worse reducibility in comparison with those obtained by calcination of coprecipitated precursors; it could be explained by a high structure ordering of the formed oxide phases. The deposited mixed oxides containing Cu showed reduction peaks at relatively low temperatures (250 – 300°C) and consequently also a reasonable catalytic activity in total oxidation of ethanol.

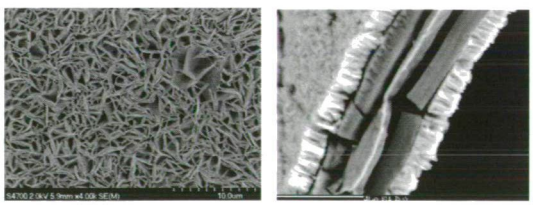

Fig. 1: SEM images of the deposited Co-(Mn)-Al LDH layer (left) and profile of the calcined sample (right).

Acknowledgements: This work was supported by the Czech Science Foundation (P106/10/1762 and 106/09/1664) and by the Ministry of Education, Youth and Sports of the Czech Republic (MSM 6046137302).

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Hydrothermal synthesis of Al-Fe^{3+} smectites: a crystal chemistry study

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Synthesis in laboratory allows control of the chemical makeup and the conditions for crystallization of clay minerals. Clay synthesis is then a useful approach for understanding natural clay minerals formation. Well defined samples having distinct chemical composition in series can be synthesized which are well suited for spectroscopic interpretations.

A series of Al-Fe^{3+} smectites with a wide range of chemical compositions have been synthesized for the first time. These smectites were synthesized by hydrothermal treatments from coprecipitated gels. The hydrothermal syntheses were performed at different temperatures and pHs. For Fe^{3+}-rich smectites, low temperature and relatively basic pH conditions are suitable whereas for Al-rich smectites, higher temperatures and more acidic pHs are appropriate [1].

These smectites have been analyzed by X-Ray Diffraction (XRD), infrared (IR in the near and the middle region, respectively NIR and MIR), Extended X-ray Absorption Fine Structure (EXAFS at the Fe K-edge and Fe L-edge) and Nuclear Magnetic Resonance (NMR) spectroscopies. Chemical analyses of the smectite particles have been performed using Transmission Electron Microscopy (TEM) equipped with an EDX (Energy Dispersive X-ray) system.

The smectitic nature of the synthesized samples is confirmed by their swelling behavior after ethylene-glycol treatment measured by XRD on oriented deposits. MIR and NIR spectra reveal variations of the relative intensities of the $Fe^{3+}{}_2OH$, $AlFe^{3+}OH$ and Al_2OH bands all along the chemical series indicating the crystal-chemical changes in these smectites in response to composition. Fe K-edge spectra reveal the presence of Fe in tetrahedral sites in the Fe-rich smectites. Fe L-edge spectra were fitted using ferrite spectrum as Fe(III) tetrahedral reference and NAu-1 nontronite as Fe(III) octahedral reference to obtain the percentage of Fe(III) in the different sites. The percentage of tetrahedral Fe(III) in these samples globally decreases with increasing Al in the structure.

^{27}Al MAS NMR spectra were recorded even for smectites very rich in iron providing information on at least some of the site occupancies (Al(4)/Al(6)) depending on the synthesis conditions.

[1] Andrieux, P. & Petit, S. (2010) *Appl. Clay Sci.*, **48**, 5-17.

"Mauritzite": a ferro/ferri-saponite transforming by immediate in-situ oxidation in dacite cavities, Erdőbénye, Hungary

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The pyroxene dacite laccolith of Mulató Hill (Erdőbénye, Tokaj Hills, NE-Hungary) formed as part of the Neogene Inner-Carpathian volcanic chain. Quarried since 1925, the laccolith is well-known for its hydrothermal cavity-filling mineral assemblage [1]. Amygdules host among others siderite, tridymite, chalcedony and an iron-rich saponite. Saponite is a cavity-lining, mostly vermicular phase forming few-mm-long fibres of ca. 0.1 mm diameter. It is mid-blue when the host cavity is opened (i.e., when first gets into contact with air), but rapidly (few ten minutes) darkens and finally turns bluish black due to in-situ oxidation.

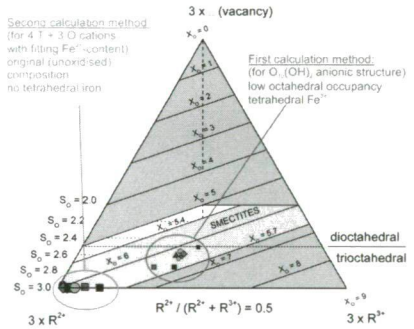

Fig. 1: Ternary diagram showing the composition of the octahedral sheet of the studied smectite. S_O = octahedral site occupancy; X_O = octahedral cation charge; R^{2+}, R^{3+} = octahedral cations.

The subhedral crystallites are up to 500 nm wide and a few nm thick, and exhibit the typical ring-like diffraction pattern of smectites. Mössbauer spectroscopy revealed that 90% of the iron content is Fe^{3+}. Tetrahedral Fe^{3+} was excluded. Calculating the crystal chemical formula from TEM-EDX data and 10% Fe^{2+}, for $O_{10}(OH)_2$ anionic structure, octahedral occupancy was found to be low (2.6 *a.p.f.u.*) and the tetrahedral sites had 0.2 *a.p.f.u.* Fe^{3+}, contradicting Mössbauer data. If modelling the original, unoxidised state of the mineral, calculating the formula for 4 tetrahedral + 3 octahedral cations, fitting iron oxidation state to retrieve an electrostatically neutral formula, 90-97% of Fe is Fe^{2+}, and there is no iron in the tetrahedral positions. It is suggested that the iron-rich trioctahedral smectite has originally around 90% of its iron content in the divalent form, which is mostly oxidised to Fe^{3+} in contact with air, accompanied by the deprotonation of the OH groups. The original (unoxidised) formula is approximately $Ca_{0.15}K_{0.04}(Mg_{1.5}Fe^{3+}{}_{0.14}Fe^{2+}{}_{1.37}Al_{0.1})[Si_{3.5}Al_{0.5}O_{10}](OH)_2$, while the oxidised one is approximated as $Ca_{0.15}K_{0.04}(Mg_{1.5}Fe^{3+}{}_{1.37}Fe^{2+}{}_{0.14}Al_{0.1})[Si_{3.5}Al_{0.5}O_{10}]O_{1.23}(OH)_{0.77}$. Based on the calculated chemical formula, the oxidised form and partly the unoxidised form (where Fe^{2+} > Mg) can be regarded as new smectite species.

[1] Papp, G. et al. (1993) (eds.) *Topographia Mineralogica Hungariae*, **1**, 1-89.

Structure modeling and its application to the analysis of crystal-chemical variations in dioctahedral micas

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An improved structure modeling procedure has been elaborated for the calculation of atomic coordinates in dioctahedral micas from the experimental data on cation composition and unit-cell parameters. The algorithm is based on regression equations relating the structural features and chemical composition of dioctahedral micas that were obtained from the analysis of published data on refined structures of micas of various compositions. The new technique follows the general approach [1], but in order to account for new high-precision refined structural data on dioctahedral $2M_1$ micas published since 1993 the majority of regression equations were modified. In addition, changes were made in the calculation algorithm.

The empirical relationships used in the algorithm accurately describe the observed structural distortions in dioctahedral micas, such as tetrahedral tilt and rotation, tetrahedral elongation, octahedral flattening; hydroxyl depression *etc.*, and include the following dependences:

mean tetrahedral and octahedral bond lengths, d_T and d(M-O,OH) *vs* tetrahedral and octahedral cation composition, respectively;

differences between non-bridging and bridging tetrahedral bond lengths, d_{nbr} and d_{br} *vs* cation composition;

differences between distances from the octahedral cation to hydroxyl and non-hydroxyl oxygen anions, d(M-O) and d(M-OH), *vs* cation composition;

tetrahedral sheet basal surface corrugation, ΔZ, *vs* d(M-O) and b;

tetrahedral sheet thickness calculated over non-depressed basal O anions, $h_{T,max}$, *vs* ΔZ;

tetrahedral mean basal edge length, l_b, *vs* tetrahedral and interlayer cation composition;

tetrahedral elongated basal edge length, l_{bl}, *vs* octahedral cation composition;

tetrahedral ditrigonal rotation angle, α_T, *vs* l_b and b;

mean octahedral sheet thickness, $<h_{oct}>$, *vs* octahedral cation composition and b;

hydroxyl depression, Δ_{OH}, *vs* octahedral cation composition;

octahedral cation shift in dioctahedral $2M_1$ micas *vs* octahedral cation composition.

The estimated standard deviations are 0.002-0.007 Å for distance parameters and 0.5° for α_T

Structure modeling was used to deduce atomic coordinates for several low-temperature $1M$ dioctahedral micaceous minerals from solid solutions (Mg, Fe)-free illite-aluminoceladonite via Mg-rich illite and Fe^{3+}-rich glauconite-celadonite, for which structure studies are problematic because of fine dispersion and low structural order. The application of the structure modeling procedure to these samples was based on the assumption that the structural features of the 2:1 layer in $1M$ micas should be similar to those in $2M_1$, so that the structural data modeled for the $1M$ mica structures should have similar reliability. Analysis of the modeled structures revealed the basic factors responsible for crystal-chemical variations in the two sample series.

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Excess protons and tetrahedrally coordinated Ni^{2+} in triocta-dioctahedral micas

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Series of Ni-micas have been prepared by hydrothermal synthesis at 500°C, 1 kbar PH_2O, in the K_2O-NiO-SiO_2-H_2O system. A complete mica solid solution has been obtained under the chosen experimental conditions, between two end-members with the nominal compositions $K(Ni_{2.5}\square_{0.5})Si_4O_{10}(OH)_2$ [A] and $KNi_3(Si_{3.5}Ni_{0.5})O_{10}(OH)_2$ [B]. The [A] phase is a triocta-dioctahedral mica, with 50% OH groups bonded to three Ni^{2+} and 50% bonded to two Ni^{2+} and adjacent to an octahedral vacancy. At the [B] end-member, Ni^{2+} is present in both [6] and [4] coordination numbers, which is an uncommon situation. Along the join, the mica color reflects the evolution of the composition, from pale green for [A], which contains only $[6]Ni^{2+}$, to sky blue for [B].

Both UV-vis and FTIR spectroscopies confirm the presence of $^{[4]}Ni^{2+}$ besides $^{[6]}Ni^{2+}$. In UV-vis, the first transition ν_1(t): $^3T_1$ (F) → $^3T_2$ (F) is outside the observable range. ν_2(t): → 3A2 (F) is at 9078 cm^{-1} and ν_3(t): $^3T_1$ (P) includes two bands at 15280 and 17120 cm^{-1}. CFSE Δ_t and Bt were calculated as 4910 cm^{-1} and 887 cm^{-1}, respectively. From these data, ν_1(t) was derived as 4160 cm^{-1}. FTIR spectroscopy in the antisymmetric T-O-T region, around 1000 cm^{-1}, also demonstrates the presence of $^{[4]}Ni^{2+}$. The [A] end-member shows two bands in this region, a high intensity band at low wavenumber, 970 cm^{-1}, due to the antisymmetric Si-O-Si motion, and a low intensity one, at 1120 cm^{-1}, assigned to the Si-O ⊥ vibration. Towards [B], a second doublet appears, at 1020 and 1080 cm^{-1}, also assigned to T-O-T and Si-O ⊥ vibrations but involving SiO_4 adjacent to NiO_4 tetrahedra.

Along the [A]-[B] join, vacant octahedral sites and NiO_4 tetrahedra, both generating local charge imbalances, are expected to be as far as possible from each other. On the contrary, they are systematically associated which provokes a strong charge imbalance on the apical oxygens of NiO_4 tetrahedra. These local defects are compensated by the incorporation of additional protons, very strongly bonded to the structure. FTIR spectroscopy in the OH stretching region confirms the presence of $^{[4]}Ni^{2+}$ and excess protons. The spectrum of the [A] mica mainly shows two bands, at 3677 and 3543 cm^{-1}, due to OH-groups in trioctahedral (Ni_3) and dioctahedral ($Ni_2\square$) environments, respectively. Along the [A]-[B] join, the IR spectra become more and more complicated in this region, and up to six bands are observed, from 3664 cm^{-1} to 3507 cm^{-1}, corresponding to the different combinations Ni_3-OH, $Ni_2\square$-OH in the octahedral layer plus Si-O-Si and Si-O-Ni in the tetrahedra. This very low wavenumber band is assigned to remaining dioctahedral OH-groups bonded to $2^{[6]}Ni^{2+}$ pointing towards $^{[4]}$Si-O-$^{[4]}$Ni tetrahedral associations. A broad grows at high wavenumber, 3635 cm^{-1}, as $^{[4]}Ni^{2+}$ content increases in the solid solution. It is assigned to the additional OH-groups.

Finally, a clear 1:1 correlation is observed between $^{[4]}Ni^{2+}$ and the additional H^+ content, measured by thermogravimetric analysis. We conclude that the [B] mica is off-composition. The structural formula of the corresponding compound can be written $K(Ni_{2.75}\square_{0.25})(Si_{3.5}Ni_{0.5})O_{9.5}(OH)_{2.5}$.

Characterization of the interlayer space of synthetic micas by far infrared spectroscopy

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Series of synthetic mica solid solutions, related to phlogopites, have been characterized by far infrared absorption spectroscopy in order to derive the influence of octahedral, coupled tetra- and octahedral, and anionic substitutions on the properties of the interlayer site and specially on the interactions between the compensating cation and the basal oxygens of the tetrahedral layers.

In the far infrared region (wavenumbers < 200cm^{-1}), three main groups of bands can be observed: (1) a band at ν > 150 cm^{-1}, frequently broad with several shoulders, and sometimes well resolved, like in talc with a doublet at 177 and 166 cm^{-1}. The wavenumber of this band, or doublet, is sensitive to the nature of the octahedral cation and its assignment is beyond the scope of this work. (2) a plus or minus broad band, in the range 140-130 cm^{-1} and (3) a low-wavenumber band, with ν < 110 cm^{-1}. The last two bands evidently involve the interlayer cation C, first because they are absent in talc and second because they shift as a function of the nature of this cation (mass and charge effect). Previous measurements on oriented single crystals led to assign the first band(s) to out-of-plane C-O motions, roughly along the c* direction, and the low-wavenumber band(s) to in-plane C-O vibrations.

The micas investigated belong to the joins phlogopite $KMg_3(Si_3Al)O_{10}(OH)_2$ - $KM^{2+}{}_3(Si_3Al)O_{10}(OH)_2$, with M^{2+} = Fe^{2+}, Co^{2+} and Ni^{2+}, phlogopite - eastonite $K(Mg_{2.5}Al_{0.5})(Si_{2.5}Al_{1.5})O_{10}(OH)_2$, phlogopite - tetrasilicic Mg mica (TMM) $K(Mg_{2.5}\square_{0.5})Si_4O_{10}(OH)_2$, and their OH^- - F^- substituted equivalents, plus trioctahedral Na-micas along the join aspidolite $NaMg_3(Si_3Al)O_{10}(OH)_2$ - preiswerkite $Na(Mg_2Al)(Si_2Al_2)O_{10}(OH)_2$.

The low-wavenumber band (in the range 110 - 80 cm^{-1}) is particularly sensitive to variations of crystal-chemical features. A systematic correlation is observed between the geometry of the interlayer site and the position of this band. The main factor is the ditrigonal distorsion of the tetrahedral layer, measured by the α angle. This distortion is required to compensate the misfit between tetrahedral and octahedral layers and can be measured by XRD. It depends on the tetrahedral and octahedral occupancies: $^{[4]}$(Si,Al) proportion and ionic radius of the $^{[6]}$M cation(s) and varies from $\approx$ 1° in annite (the Fe^{2+} equivalent of phlogopite), to 20° in preiswerkite. In all series, the wavenumber of the in-plane C - O vibration increases with α, indicating higher C - O bond strengths, and a better retention of the interlayer cation.

The evolution of out-of-plane vibration(s) with composition is less clear. Generally the trend is in the reverse way, and frequently this band overlaps with the higher wavenumber ones, see (1). Nevertheless their evolution also reflects crystal-chemical modifications in the interlayer space.

Application of XANES experimental and theoretical studies to high-coordination cations. The case of potassium in micas

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Polarized synchrotron radiation allows recording angle-dependent XANES (AXANES) spectra of layered minerals, such as trioctahedral 1*M*-micas [1,2]. The experimental spectra can be evaluated for both their in-plane and out-of-plane component fractions of the electric dipole contribution, so that the related multiple-scattering pathways can be extracted. Most contributions arise from multiple-scattering interactions of the photoelectron ejected from the absorber (K in the interlayer *I*) colliding with other coplanar K and/or alkali atoms, and also with facing oxygen atoms that lie on the basal planes of the tetrahedral *T* sheets [3]. By contrast, the out-of-plane component fractions arise from multiple-scattering pathways that cross the energetic and structural barrier represented by the *T* sheets and reach the *W* anions that are located on the upper level of the octahedral *M* sheets and also the metal cations centering the *M* sheet itself. *Ab initio* calculations help to further interpolate experimental angle-dependent XANES work and to deduce from it the related physical/chemical effects. Calculations show that there are unexpected, large distortions in the mica local structure around the K atoms of the interlayer *I*. Such structural distortions are highly correlated with the compositional disordering that arises from electronic interactions between anions and cations, and extend far away *I* entering deep into the nearby *T* and *M* sheets [4].

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Kaolinite and dickite behaviour after deformation by compaction and shear

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The structural changes produced on commercial powdered kaolin deformed by compaction and shear was investigated by X-ray diffraction (XRD), low temperature FTIR, differential thermal analysis and thermogravimetry (DTA/TG). Kaolin is composed by 40% of well orderered kaolinite, 18% of dickite and 42% of quartz. The deformation was induced through a specifically built planetary ball milling working in a controlled thermodynamic environment at room temperature and at a vacuum of 0.13 Pa (10^{-3} Torr). In this controlled environment the mechanical apparatus induces simultaneous compaction and shear stress to the material as described in detail by [1]. Kaolin samples were milled for 1, 5, 10 and 20 hours.

The deformation treatment produces a kaolinite structural order decrease, from a low-defect kaolinite to a high-defect kaolinite according to the AGFI index determined by XRD [2]. An index to evaluate the changes produced on dickite was determined following the fitting procedure described in [2]. The results indicated that dickite is apparently less affected by the deformation than kaolinite. A structural order was defined by FTIR and the results were correlated with AGFI results.

Low-temperature FTIR spectral analysis of kaolin group minerals provides a sensitive method for detecting the presence of kaolinite, dickite and nacrite [3]. Using this technique it was confirmed that dickite is more resistant to the deformation process than kaolinite. This technique indicates also that the deformation process produces a hydrous phase which increases with the time of the treatment and, at the same time, that kaolin minerals decrease (Fig.1). The presence of this hydrous phase was also confirmed by DTA/TG, which indicates that its percentage increases especially after 5 hours of treatment.

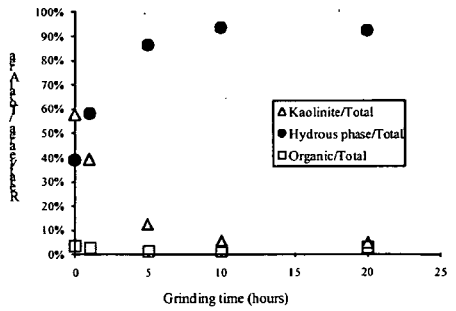

Fig. 1: Evolution of kaolinite and hydrous phase, determined by low temperature FTIR, versus time of deformation process.

In summary our peculiar milling induced a structural change to the octahedral sheets of kaolinite and subsequently to the tetrahedral ones. A progressive reduction of the stacking layer coherence is observed, although the complete amorphisation was not induced even after prolonged milling for 20 hours. Dickite remains after the deformation treatment by compaction and shear even for long times.

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Synthesis and degradation mechanism of a swelling fluoromica

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Na-2-mica, a synthetic swelling fluoromica, has recently attracted much attention for its unique combination of high charge (2 charges per unit cell) and its capacity to expand and exchange cations from the interlayer space. A variety of studies regarding the exchange and retention properties of those fluoromicas have been published, as well as their applications in the decontamination of soils [1,2]. However, few studies have been devoted so far to clarify key aspects such as the formation mechanism, the local order of the tetrahedral cations and the arrangement of interlayer species [3-5].

It is well-known that the distribution of aluminum in the framework, and thus the local framework negative charge, would have a dramatic effect on the properties of aluminosilicates [6,7]. If Al distribution in synthetic aluminosilicates could be adjusted, it would offer a way to control their properties. To achieve an exhaustive control of Al distribution through the conditions of synthesis, an experimental method for the determination or, at least, for indirect estimation of the distribution of aluminum in the aluminosilicate framework should be available.

The objectives of this research were to synthesize fluoromica at variable reaction times between 0 and 600 hours. That could enable us to determine the optimum reaction time for the process and identify the appearance of intermediate species which inform of the reaction mechanism. At the same time, the local order changes accompanying the synthesis process, which influence the final physico-chemical properties of the product, could be analyzed.

With the combined use of techniques that inform of both the long and short range structural order, we have shed a light on the synthesis mechanism of high-charge swelling mica and its stability range. The precursors are rapidly transformed into intermediate phases such as tectosilicates and 2:1 phyllosilicate. The precursors are transformed into fluoromica which remains stable for a period of time. Finally, the fluoromica starts to decompose and only the firing products are present.

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Surface structure of natural muscovite

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The aim of this project is to study the atomic surface structure of a natural muscovite crystal by means of the synchrotron radiation light and the grazing incidence X-ray diffraction (GIXRD).

The muscovite studied [$(K_{0.92}Na_{0.08})$ $(Al_{1.86}Fe^{3+}_{0.01}Mg_{0.07}$ $Fe^{2+}_{0.06}Ti_{0.02})$ $(Si_{3.03}Al_{0.97})$ O_{10} $F_{0.09}$ $(OH)_{1.91}$] is monoclinic, $2M_1$ polytype, with space group $C2/c$ and unit cell parameters: a = 5.19690(10), b = 9.0138(3), c = 20.0835(7) Å, β = 95.763(2)°.

The muscovite structure was refined by single crystal X-ray diffraction and the final refinement yielded the agreement factor R = 0.0299. The difference Fourier map shows a significant residual electron density (2.2 e^-) close to the position related to the M1 site, thus indicating that the excess of octahedral cations is located at M1. The <M1-O> mean bond distance is 2.247(9) and the <M2-O> distance is 1.929 Å.

Grazing incidence X-ray diffraction (GIXRD) was recently performed at SpLine at the European Synchrotron Radiation Facility (ESRF). This type of analysis is very useful to identify typical structural features of the surface, such as possible imperfections, relaxations or reconstructions [1]. Usually, the atoms on surfaces, and sometimes those as deep as several layers down, assume positions different from their equilibrium positions in the bulk. Generally mineral surfaces will not be reconstructed unless they have been heated to temperature higher than 100°C [2]. In our case, the muscovite surface has been exposed to a delay of the first layer in order to study a freshly cleaned surface and data collected by GIXRD confirm that on muscovite surface only a relaxation occurs from an equivalent plane in the bulk. This is a common case for minerals with a low-symmetry structure, e.g. for feldspar [3].

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Preparation of homoionic exchanged smectites in bentonites: influence of cation valence and soluble minerals on the success of exchange

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The interlayers of natural smectites are commonly occupied by a mixture of Na^+ and/or Ca^{2+} and Mg^{2+}, respectively, and to less extent by K^+. Many chemical, mechanical and thermal properties of smectites and smectite-rich materials depend on the interlayer cations. Therefore, homoionic exchanged materials are prepared to investigate reaction mechanism as function of the interlayer cation or as function of the layer structure with uniform interlayer occupation. 54 publications from different journals from 1950 to 2009 were reviewed with respect to the applied homoionic exchange procedure. Only 6 papers [1-6] reported on the success of homoionic exchange. Up to now there exists no general instruction to prepare homoionic exchanged smectites in dependency of layer charge, cation exchange capacity (CEC) and the obtained level of homoionic interlayers. The aim of the present study was to create a general instruction based on smectite properties, overall phase content and experimental conditions.

For the research three natural bentonites were applied, which differ in content of calcite, dolomite, and gypsum and whose smectites differ in layer charge, CEC and interlayer composition. The homoionic exchange was achieved by repeated reactions of air dry clay aliquots with suspensions of readily soluble chlorides of different cations (Na, Li, K, Mg, Ca, and Cu). The concentration of the chloride solutions was equal to 1x CEC, 5x CEC, 10x CEC and 20x CEC of each material. The solid-liquid ratio averaged 4.4%. The success of homoionic exchange was monitored by exchange of interlayer cations with Cu-Trien and subsequent analysis of the cations in the supernatant exchange solution by ICP-OES.

As expected from charge, size and hydration properties of the cations the homoionic exchange with bivalent cations (Mg, Ca, and Cu) was more effective compared to that with monovalent cations (Na, Li, and K). In addition the exchange of monovalent cations was strongly inhibited or even prevented during exchange experiments with low salt concentrations (1-5x CEC) by present carbonates and sulfates that were dissolved during the exchange reactions. The released Ca or Mg replaced the monovalent cations in the interlayer, thus, the amount of Ca and Mg increased compared to the starting material.

The homoionic exchange was regarded successful if more than 95% of the interlayer consists of a single type of cation. To reach this occupancy rate, 20x CEC (three times exchange) was necessary for monovalent cations and 5x CEC (three times exchange) for bivalent cations. Purification improved the uptake of monovalent cations (reduced concentration of exchange solution, e.g. 5x CEC for K).

Our results briefly indicate that the following information: layer charge, CEC, solid-liquid ratio, concentration of salt solution, type of salt, reaction time, repetitions, and success of exchange should be reported as exchange procedure differs for materials in dependence of material properties, pretreatment and experimental conditions to enable comparison of different studies.

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Structural and crystallochemical characterization of sepiolites

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Sepiolite is a hydrous Mg-rich silicate clay mineral with fibrous morphology that typically occurs as fine-grained, poorly crystalline masses. It is an important industrial mineral with more than 100 commercial uses today in the pharmaceutical, fertilizer, and pesticide industries [1].

In this study, we report the structural and crystallochemical characterization of two sepiolite locations in the same geological context. This is in order to establish structure-properties relations of these clays. The materials came from a lacustrine environment in the Intermediate Unit of Miocene sediments of the Madrid basin (Spain), specifically located in the East of Madrid, Barajas - Vicálvaro.

The crystal structure of four samples of sepiolite was analysed using X-ray diffraction technique and the Rietveld structural refinement method. Sepiolites from Barajas show dolomite and quartz as accessory minerals. Crystal parameters obtained by Rietveld refinement are different depending on the origin, Barajas or Vicálvaro and are attributed to different hydration states.

Structural formulae of sepiolite samples calculated from the results of the chemical analysis, corrected by using the quantification of secondary mineral phases by Rietveld refinement, were close to the ideal formula based on the literature [2].

On the other hand, the X-ray thermodiffraction study revealed zeolitic H_2O is lost during heating from 25 to 200°C; bound H_2O molecules are released completely at 750°C; and hydroxyl groups are lost above 850°C. However, the more ideal sepiolite composition is related to significant better thermal properties characterized by the maintenance of the dehydrated sepiolite structure unchanged up to 350°C. Above this T a similar evolution can be followed for the several sepiolites, ending with a phase transformation to enstatite mineral.

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Characterization of clay material from chalk reservoirs in Denmark

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The presence of clay in reservoir chalk has an effect on calcite recrystallization [1]. It has been suggested that a high clay content enhances chalk dissolution and hence calcite recrystallization [2,3]. Clay could also inhibit recrystallization when it nucleates and grows over the chalk particles. Therefore, although chalk might only contain a few percent of clay, its mineral composition, morphology, size and structure can play an important role in the properties and behaviour of the reservoir. In this study, we examined Maastrichtian age samples from the Aalborg Portland pit (Jutland, Denmark) and from a shallow borehole at Klintholm (Fyn) as well as from the North Sea basin.

Clay was separated from the chalk and analyzed using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM) and infrared spectroscopy (IR). The clay types varies from sample to sample, but there is little variation among samples from the same location. SEM and AFM show that there are two distinctly different morphologies of clay. By volume, the major part consists of detrital larger grain smectite or mixed layer smectite/illite but we also find smaller particles of clay, sometimes single layers, which have grown in pore spaces and on the surface of other chalk particles.

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Crystal chemistry and thermodynamic properties of kerolite-stevensite mixed-layer minerals

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Two kerolite-stevensite mixed-layer minerals from residual soils of serpentinized ultra basic rocks (Ural, Russia) are studied by X-ray diffraction (XRD), infrared spectroscopy (FTIR), differential thermal (DTA), thermogravimetric (TG, DTG), electron microprobe, and thermochemical analyses. The FTIR-spectra of both air-dried samples indicate that these belong to kerolite-pimelite-trioctahedral smectite minerals with different levels of Ni for Mg substitution [1-3]. This is confirmed by XRD modeling, which additionally shows a mixed layer structure with ca. 30-40% expandable layers. Both samples in air-dried state exhibit the 001 reflection at 11.6 Å shifting to 9.7 Å upon heating at 550-600°C. The corresponding patterns of the ethylene-glycolated samples depend on Ni content (25.0, 13.0, 9.3, 5.3 Å and 24.0, 17.0, 9.0, 5.3 Å for the Ni-poor and Ni-rich samples, respectively).

The TDA and TG curves of both samples are similar and show three steps of water loss: 100-200°C – adsorption water (7.5 and 7.7%) with t_{max} = 100°C, 200-780°C – structural water (2.8 and 3.5%) with $t_{max} \approx$ 380°C, and 780-1050°C – dehydroxylation (4.3 and 3.8%) with t_{max} = 850°C, for the Ni-poor and Ni-rich samples, respectively. Chemical formulas calculated on the basis of a +22 total cation charge were:

$[(Mg_{2.91}Ni_{0.02}Fe_{0.02}Al_{0.01})Si_4O_{10}(OH)_2][Na_{0.02}Ca_{0.02}] \cdot 0.7H_2O$ (I), $[(Mg_{2.07}Ni_{0.87}Fe_{0.08}Al_{0.04})\ (Si_{3.76}Al_{0.24})\ O_{10}\ (OH)_2]\ [Na_{0.02}Ca_{0.03}] \cdot 0.9H_2O$ (II).

Thermochemical investigations by "transposed temperature drop solution calorimetry" are performed in molten $2PbO \cdot B_2O_3$ at T=973 K with a Tian-Calvet high-temperature heat-flux calorimeter. The calibration of the calorimeter was performed by dropping pieces of platinum wire with known enthalpy increments, and the sum of the heat of solution and the heat content of the sample was measured: $\Delta H = [H^o(973\ K) - H^o(298.15\ K) + \Delta H_{sol.}973\ K)]$. The enthalpies of formation from the elements of the kerolite-stevensite mixed-layer minerals were determined after corrections for adsorbed water and by employing reference data for the constituent oxides according to the equation: $\Delta_f H^o_{el}(298.15\ K)_{min.} = \sum v_i \Delta H_{oxi} - \Delta H_{min.} + \sum v_i \Delta_f H^o_{el}(298.15\ K)_{oxi}$, where v_i are the stoichiometric coefficients in the reaction of mineral formation from the oxides. The resulting $\Delta_f H^o_{el}(298.15\ K)$ values are -6018.4±8.5 $kJ \cdot mol^{-1}$ for the Ni-poor sample (I) and -5823±14 $kJ \cdot mol^{-1}$ for the Ni-rich sample (II). These values suggest that the Mg-rich members of the kerolite-stevensite mixed-layer minerals are more stable than their N-rich analogs.

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Crystallization of natural montmorillonite applying very-high pressure and temperature

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Clay minerals of the smectite group are inorganic materials with ability to react with organic compounds. For this reason, they attract particular attention for their application as nanohosts for organic guest molecules. However, smectite occurs usually as a poorly crystallized fine powder. Their characterization and application have been hindered by a lack of large single crystals.

An entropy consideration suggests that a 3D-ordered smectite, if it would exist, might be stable under higher pressure than smectite with a turbostratically disordered structure. Previously, one of the authors has been successful in synthesis of smectite crystals using a silica-alumina glass as starting material by applying 5.5 GPa and 1600°C [1]. However, their crystal sizes were still insufficient for an X-ray structure analysis and nothing was known about their stability relations at very high pressures and temperatures.

In this contribution, similar pressures and temperatures were applied to natural montmorillonite and a highly purified bentonite from Yamagata, Japan, as starting materials. The purification procedures and characterization have been reported in detail elsewhere [2].

The montmorillonite was placed in 100% of humidity for 24 h before the experiment and was encapsulated in a Pt tube with water of about 15 wt.%. Very high pressures and temperatures were applied to the sample by using a belt-type apparatus, e.g. 5.5 GPa and 1500°C for 1 hr [3]. A series of runs under 5.5 GPa were carried out at different temperatures in the range from 1700 to 1000 °C and for durations from 1 to 25 h.

The high pressure product was lightly crushed, mounted on a glass slide, observed by optical microscope and studied by X-ray diffraction for identification. The sample was then exposed to ethylene glycol vapour for one night and investigated again for confirmation of characteristic expansion of smectite. Its morphology was observed by electron microprobe analyzer (JEOL, JXA-8500F) and transmission electron microscope (JEOL, JEM 2000EX).

X-ray diffraction (XRD) study showed that the products consist mostly of montmorillonite with small admixture of kyanite. All the XRD peaks of montmorillonite were extremely sharp. Morphologies of particles revealed in the SEM and TEM images corresponded to long euhedral laths and rare hexagonal thin plates.

Because the starting montmorillonite was extremely fine nanometer-scale powder and completely disordered from structural viewpoint, the euhedral morphology of the high pressure montmorillonite and its size of some tens of micron meter indicate that they were surely grown under high pressure and temperature, probably by the Ostwald ripening mechanism. This suggests that there may be a stable phase of 3D-montmorillonite at very high pressure and temperature around 5.5 GPa and 1700°C. The synthesis of large single crystals of montmorillonite is therefore not entirely impossible and seems to be rather realistic.

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How to calculate mineral formula for 3-members mixed layers from EDX-analysis by Transmission Electron Microscopy: example – kaolinite-smectite-vermiculite mixed layers in Friedland Clay (Germany)

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Transmission electron microscopy (TEM) is a very sensitive tool to recognize alteration processes of montmorillonite or other clay mineral phases. The variability of chemical composition of interlayer space, octahedral as well as tetrahedral sheets of each TEM-EDX investigated particle is mirroring this process of alteration.

The contribution offers a methodology to calculate the mineral formula also from particles, which represents e.g. irregular interstratified mixed layer structures with three end members composed by kaolinite, smectite and dioctahedral vermiculite (KSV-ml).

For the calculation of a model mineral formula of KSV-ml it was developed a series of equations to convert the TEM-EDX-analysis of each particle. This conversion is controlled by three parameters: (i) total charge (22 ... 28 per $(OH)_n$ O_{10}), (ii) Si-amount in tetrahedral sheet and (iii) numbers of atoms in octahedral sheet (2 ... 4 per $(OH)_n$ O_{10}).

The contribution contains also an approach of this methodology for the German Friedland clay. Friedland clay is composed mainly by Fe-rich illite-smectite mixed layer (IS-ml), kaolinite (15 wt.%), mica, quartz. KS-ml or KSV-ml could be not detected there before by XRD. After deconvolution of XRD-traces (oriented mounts: air dried, ethylene-glycol saturation) by BGMN-Rietveld technique X-ray diffraction of Friedland clay confirms now also the occurrence for KSV-ml.
Applying presenting TEM-EDX-methodology following different compositions of KSV-ml were calculated in three different samples of Friedland clay. Each analysed sample of Friedland clay is representing a different geological history.

KSV-ml in Friedland Clay 1 *(%K 60%, %S 25%, %V 15%)*
$Mg_{0.01}Ca_{0.02}Na_{0.05}K_{0.08}Al_{2.96}Fe^{3+}_{0.13}Mg_{0.08}Ti_{<0.01}(OH)_{5.54}$
$Si_{3.90}Al_{0.10}O_{10}]$
KSV-ml in Friedland Clay 2 *(%K 45%, %S 40%, %V 15%)*
$Mg_{0.03}Ca_{0.01}Na_{0.03}K_{0.06}Al_{2.76}Fe^{3+}_{0.11}Mg_{0.03}Ti_{<0.01}[(OH)_{4.72}$
$Si_{3.88}Al_{0.12}O_{10}]$
KSV-ml in Friedland Clay 3 *(%K 50%, %S 35%, %V 15%)*
$Mg_{0.02}Ca_{0.02}Na_{0.00}K_{0.06}Al_{2.64}Fe^{3+}_{0.24}Mg_{0.03}Ti_{<0.01}[(OH)_{4.79}$
$Si_{3.89}Al_{0.11}O_{10}]$

Friedland Clay 1 represents the original composition located in the core of ore body. Friedland Clay 2 shows alterations by interaction with glacial water in a closed system. Friedland Clay 3 mirrors the effect of rain to the clay mineral matter (Clay 2) at the surface of open cast mine (= open system).

The differences between Clay (1) and (2) are comparable with smectitization. The differences between Clay (2) and (3) are pronounced by higher octahedral Fe3+ in substitution of octahedral Al. The origin of Fe is the result of degradation processes of Fe-rich IS-ml phases and oxidation of pyrite.

KSV-ml structures in Friedland Clay undergo similar processes of alteration in closed and open systems like described for smectite by Herbert et al. (2008) [1] from batch experiments with bentonites.

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The kaolinite-dickite relation by thermodynamic data

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The thermodynamic properties of the kaolinite $Al_2Si_2O_5(OH)_4$ and its polymorph dickite were studied on natural samples of kaolinite from the Glukhovetskoye (Ukraine) and dickite from Tibskoye deposits (Russia). Samples were characterized by optical microscopy, X-ray diffraction, electron probe microanalysis, infrared spectroscopy (FTIR) and differential thermal and thermogravimetric analyses. The XRD data refined by Rietveld method with QUANTO software [1] showed rather purity of both studied samples (kaolinite – more 96%, dickite – more 92%). They were well-crystallized, the IR-absorbance spectra and the thermal curves correspond to pure minerals. All thermodynamic investigations were performed with a Tian-Calvet high-temperature heat-flux calorimeter ("Setaram", France). The enthalpies of formation from the elements were determined by "transposed temperature drop solution calorimetry" in molten $2PbO \cdot B_2O_3$ at T=973 K. The sum of the heat of solution and the heat content of the sample was measured:

$$\Delta H = H^\circ(973\ K) - H^\circ(298.15\ K) + \Delta H^\circ_{solution}(973\ K).$$

Before experiments, all samples were heated at 200°C for 1.5 hours to remove minor amount of low-temperature water. Calibration of the calorimeter was performed by dropping pieces of platinum wire with known enthalpy increments [2]. With the calorimetric data obtained and needed thermochemical [3, 4] and reference [2] data for pyrophyllite, corundum and quartz the standard enthalpies of formation of natural minerals of kaolinite group from the elements were calculated on the basis of reaction:

$$2Al_2Si_4O_{10}(OH)_2 = Al_2Si_2O_5(OH)_4 + Al_2O_3 + 6SiO_2.$$

For the calculation the following equation was used:

$$\Delta_f H^\circ_{el}(298.15\ K)_{mineral} = 2\Delta H_{pyrophyllite} - \Delta H_{mineral} - \Delta H_{corundum} - 6\Delta H_{quartz} + 2\Delta_f H^\circ_{el}(298.15\ K)_{pyrophyllite} - \Delta_f H^\circ_{el}(298.15\ K)_{corundum} - 6\Delta_f H^\circ_{el}(298.15\ K)_{quartz},$$

where ΔH – calorimetric data for all constituent minerals. The resulting values of $\Delta_f H^\circ_{el}(298.15\ K)$ are -4118±10 kJ mol^{-1} for kaolinite and -4127±10 kJ mol^{-1} for dickite. Taking into account the reference data on their entropies [2] the Gibbs energies of formation from the elements were calculated: -3796±10 kJ mol^{-1} and -3805±10 kJ mol^{-1}, respectively. These results show that kaolinite is metastable relative to dickite and agrees with data from [5]. The more widespread natural occurance of kaolinite vs. dickite is due to kinetic factors rather than thermodynamics.

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Theoretical study of one-layered kaolinite polytypes

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The stacking of adjacent kaolinite-type structural layers with one-layer periodicity is studied using **R** vector and „+", „–" notation introduced by Dódony [1] for trioctahedral TO phyllosilicates. In this notation, **R** is the projection of the **c** axis onto the **ab** plane and „+" or „–" signs the slant of octahedral sheet. The length of **R** can be 0, **a**/3 and **b**/3, with directions of <100>, <110> for **a**/3 shifts and <010>, <310> for **b**/3 shifts, relating subsequent layers.

In the present work, all the twenty crystallographically different one-layer kaolinite polytypes allowed by H-bonding are derived as a result of possible combinations of **R** and slant of octahedral sheet („+", „–"). The number of polytypes, which is 20 (including 8 enantiomorph modifications), is in disagreement with previosuly reported 6 one-layered polytypes [2,3].

Each polytype is characterized by simulated X-ray powder diffraction pattern, [001] selected area electron diffraction (SAED) pattern and [001] projected charge density map. All simulations were calculated for the chemical composition of $Al_2Si_2O_5(OH)_4$, and with the structural dimensions of a = 5.023 Å, b = 8.700 Å, the *layer thickness* ($d_{(001)}$) = 7.000 Å and γ = 90°.

Patterns of the [001] projected charge density map of non-enantiomorph polytypes (12) differ from each other, because they are crystallographically different. By comparison of simulated data, every non-enantiomorph polytype can be identified by combination of intensity distributions and geometry of XRD and [001] SAED patterns.

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Molecular simulations of layered double hydroxides (LDHs) by various porphyrine molecules

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Molecular simulations were applied for structure analysis of Mg_2Al LDH (original nitrate form) intercalated with [5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin (TPPS)] [1] and Pd-TPPS. LDH was prepared with an Mg/Al molar ratio of 2. The results are supported by experimental methods like powder X-ray diffraction (XRD) analysis, infrared (IR) spectroscopy and thermogravimetry.

In the case of TPPS, three different types of structures were modelled. The experimental XRD patterns of LDH intercalated with TPPS show 70–80% loading with respect to the theoretical anion exchange capacity (AEC). Type 1 model represent single-phase systems with a 100% TPPS loading in the interlayer space, type 2 show the coexistence of two separate phases, the first phase has interlayer saturated with TPPS anions and the second phase has interlayer fully occupied with NO_3^- anions. Total loading of TPPS in type 2 models was in the interval of 75 – 92 %. Type 3 model represent a structure with the coexistence of both TPPS and NO_3- anions in the same interlayer space. The agreement between experimental and calculated X-ray diffraction patterns and energy characteristic of models show type 2 as most probable.

In the case of Pd-TPPS two models with various loadings (10% and 100%) were investigated. Geometry of Pd-TPPS was optimized by *ab initio* calculations. Optimized geometry of this molecule was inserted into interlayer space from parallel to nearly perpendicular arrangement. The resultant position of Pd-TPPS in the interlayer depends on the degree of intercalation and is related to AEC.

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Sonication induced reduction reactions of the Ojén (Andalucía, Spain) vermiculite

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Sonication produces a delamination and a reduction of the particle size without the significant destruction of the vermiculite structure that is caused by grinding [1]. The extent of particle size reduction and the closely related increase of the surface areas (S_{BET}) are almost independent of the choice of the transfer medium (water or a water/H_2O_2 mixture) [2]. However, chemical analysis, Mössbauer spectroscopy and infrared (IR) spectroscopy show clearly that the choice of the transfer medium can affect the structure of a particular material on a more local scale [2].

More puzzling than the oxidation in presence of hydrogen peroxide was the reduction of the Ojén vermiculite observed during sonication in pure water. Water itself does not reduce the Ojén vermiculite. Interlayer water does not play a role in the reduction of the Ojén vermiculite, since the extent of reduction is roughly the same when the potassium-exchanged Ojén vermiculite, where K^+ is almost unhydrated, is sonicated in water.

Possible reducing agents could be the $H^\bullet$ or the $HO_2^\bullet$ which are formed as an intermediate product in the sonication of (aerated) water or subsequent reactions products like H_2. Especially interesting is the $HO_2^\bullet$ radical because solid surfaces can trigger its formation [3]. Furthermore, it is well documented that these hydroperoxyl radicals react in Fenton systems even in the presence of hydrogen peroxide as a reducing agent [4,5].

To get more insight in the reduction mechanism we carried out sonication in water under air and under nitrogen. By means of Mössbauer spectroscopy we observed a significant difference: the $Fe^{3+}/Fe^{2+} + Fe^{3+}$ ratio amounts to 0.59 under nitrogen and to 0.39 under air (cf. for untreated vermiculite it is 0.73). Though under air the influence of oxygen and, thus, the contribution of $HO_2^\bullet$ cannot be neglected. Under exclusion of oxygen gaseous hydrogen cannot be the reducing agent because it does not react with the Ojén vermiculite at temperatures below 400 °C. The only other choice is the $H^\bullet$. For this radical to act on the clays as reducing agents the cavitation bubbles must be closely attached to the vermiculite surface and they have to reduce the structural iron ions prior to the recombination/decomposition to H_2 or H_2O (together with $OH^\bullet$).

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Influence of interlayer charge and water mobility on ^{29}Si NMR chemical shift of 2:1 phyllosilicates

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A series of synthetic sodium-rich saponites $Na_xMg_3(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$, with $0.33 \leq x \leq 1$ and trioctahedral Na-micas $Na(Mg_{3-y}Al_y)(Si_{3-y}Al_{1+y})O_{10}(OH)_2.nH_2O$, with $0 \leq y \leq 1$ have been investigated by ^{29}Si magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. The salient result is the major effect of the interlayer charge on ^{29}Si chemical shift of four detected NMR components ascribed to Si_3, Si_2Al, $SiAl_2$ and Al_3 environments. The contribution of the interlayer charge is much more important than the previously reported contribution of the ditrigonal distortion of tetrahedral layers, generated by the misfit between tetrahedral and octahedral layers. This observation derives from the peculiar disposition of tetrehedra in phyllosilicates, with three out of four oxygen atoms exposed to the interlamellar space. In saponites with $x < 1$, ^{29}Si MAS-NMR spectra change considerably with the amount and mobility of adsorbed water, indicating that for a given tetrahedra, chemical shift depends on the proximity and amount of interlayer charge seen by this tetrahedron. In dehydrated saponites, where Na^+ cations are disposed in ditrigonal cavities, NMR components split as a consequence of the partial occupancy of three neighbouring cavities. In hydrated saponites, chemical shifts of splitted components are averaged as a consequence of interlayer water and cation mobility. In this analysis, the effect of the increasing octahedral charge of micas is considerably lower than that of interlayer charge. In micas, chemical shift discontinuities detected near $y = 0.5$ are discussed in terms of distortions and relative disposition of contiguous layers.

Computational study of TMA^+ fluorohectorite intercalate

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The structural data of TMA^+ fluorohectorite intercalate (TMA-H) into 2:1 layer silicates suggest two possible orientations of TMA^+ cations with low occupancy (~0.9) [1]. The TMA^+ atoms could only appear in any of the positions constrained in the original space group (*C2/m*) to the 8*j* Wyckoff position. In the triclinic space group *P*1, TMA^+ cations are free to translate and rotate, though all the movements are restricted by the potential field generated by surrounding atoms. The 64 computational models of mutual orientation of TMA^+ cations were based on this assumption. The primary aim of this study is to find the energetically most favorable arrangement of the TMA^+ cations in fluorohectorite interlayer space. The second task is to identify whether a particular configuration can be detected using X-ray powder diffraction and/or vibration spectroscopy. The main tool in this study is a density functional (DFT) method as applied for the solid state in the VASP program [2]. The analysis of total energies of the models shows that approximately 70% of models fall to the region with very close energies. Hence it is very difficult if ever possible to distinguish the mutual orientation of the TMA^+ cations in these models. The calculated powder diffraction patterns for model with the lowest (BEST) and with the highest (WORST) energy confirm this result. The differences in the intensities of both patterns are almost negligible. The analysis of the calculated vibrational modes for BEST, COMMON (representing group of models with close energies) and WORST models were done in details (Fig. 1). The minimal changes in the position of the C-H stretching modes are caused by changes, formation and/or interruption of the weak C-H...O hydrogen bonds according to mutual orientation of TMA^+ cations in the models.

It can be concluded that experimental distinguishing of mutual orientations of TMA^+ cations in the fluorohectorite interlayer space by the methods discussed above is not possible.

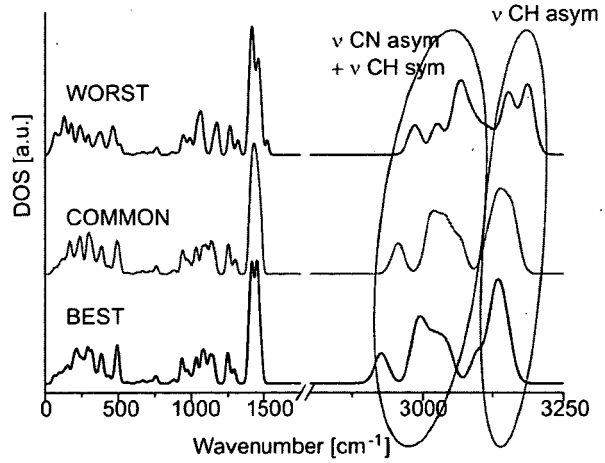

Fig. 1: The calculated vibrational density of states for selected models.

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Occlusion of sulphate salts into the Mg-Al-SO_4 hydrotalcite

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Occlusion of the different salts or molecules into the layered minerals (clays, mica), zeolites, etc. is a well known phenomenon [1]. However, there are only a few papers describing an occlusion of sulphate salts in the natural layered double hydroxides, which are also known as anionic clays or hydrotalcite-like minerals (HTs) [2-4].

This contribution presents the results of experimental investigations of occlusion (possibilities, conditions and peculiarities) of sulphate salts in the interlayer space of Mg-Al-SO_4 hydrotalcite.

Occlusion was obtained by two main ways:

1) During syntheses of the Mg-Al-SO_4 hydrotalcites (Mg:Al =2:1) by co-precipitation of mixed acid solution ($MgCl_2$ and $AlCl_3$) with mixed alkali solution (NaOH and Na_2SO_4 or K_2SO_4 in 5-fold excess). 2) Through post-synthetic reactions (sulphate solution treatment and anion exchange) of dried samples (Mg-Al-SO_4, Mg-Al-NO_3 and Mg-Al-$B_4O_5(OH)_4$ HTs) dispersed in water solutions of Na_2SO_4, K_2SO_4 or $MgSO_4$ with 5-fold excess of SO_4^{2-} anions. All obtained samples were characterized by X-ray powder diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR).

According to the literature data, lattice parameters of natural and synthetic Mg-Al-SO_4 (Mg:Al=2:1) HTs are a = 0.3044 nm and c = 2.667 nm. Table 1 lists values of the d_{003} and d_{110} reflections, which correspond to the lattice parameters $c = 3 \cdot d_{003}$ and $a = 2 \cdot d_{110}$, respectively.

Table 1: Chemical composition and cell parameters of the materials

Sample	Chemical formula	d_{003}, nm	d_{110}, nm
Occlusion during syntheses and post-synthetic treatment			
Extra Na_2SO_4	$Mg_4Al_2(OH)_{12}SO_4.mNa_2SO_4.nH_2O$	1.122	0.1522
-add. washing	$Mg_4Al_2(OH)_{12}SO_4.3H_2O$	0.889	0.1522
-above + $MgSO_4$	$Mg_4Al_2(OH)_{12}SO_4.mMgSO_4.nH_2O$	1.092	0.1525
Extra K_2SO_4	$Mg_4Al_2(OH)_{12}SO_4.mK_2SO_4.nH_2O$	1.121	0.1523
-add. washing	$Mg_4Al_2(OH)_{12}SO_4.3H_2O$	0.888	0.1523
-above + Na_2SO_4	$Mg_4Al_2(OH)_{12}SO_4.mNa_2SO_4.nH_2O$	1.121	0.1523
Occlusion through anion exchange reactions			
NO_3-HT	$Mg_4Al_2(OH)_{12}(NO_3)_2.1.5H_2O$	0.883	0.1522
-above + Na_2SO_4	$Mg_4Al_2(OH)_{12}SO_4.mNa_2SO_4.nH_2O$	1.122	0.1522
$B_3O_3(OH)_4$-HT	$Mg_4Al_2(OH)_{12}(NO_3)_2.1.5H_2O$	1.072	0.1521
-above + K_2SO_4	$Mg_4Al_2(OH)_{12}SO_4.mK_2SO_4.nH_2O$	1.122	0.1521

In the XRD patterns of the products obtained by all three types of occlusion of Na and K sulphate, the MgAl-SO_4 HTs with d_{003} = 1.12 nm were registered. These values are in agreement with previously published d_{003} values of natural MgAl-SO_4 HTs with high content of interlayer water molecules and occluded Na_2SO_4 [3]. However, after additional washing of the occluded samples, in the XRD patterns the phase with d_{003} = 0.889 nm only was observed. It can be concluded that the occlusion and extraction of the sodium and potassium sulphate salts are reversible processes and depend on the concentration of sulphate salts in the solutions and on the washing process.

In the case of occlusion of the sulphate salts of divalent cations (Mg, Ni, Zn, Co, Cd, Mn etc.) it should be taken into account the order of selectivity of divalent cations in the hydrotalcite: Mg<Mn<Cd<Co≈Ni<Zn, because the occluded cations may affect the composition of the host structure [5].

[1] Barrer, R.M (1982) *Hydrothermal chemistry of zeolites.* Academic Press, London. [2] Bish, D.L. & Livingstone, A. (1981) *Mineral. Mag.*, **44**, 339-343. [4] Drits, V.A. et al. (1986) *Clay. Clay Miner.*, **35**, 401-417. [4] Lisitzina, N.A. & Drits, V.A. (1985) *Litol. Polez. Isop.*, **6**, 20-39. [5] Stanimirova, Ts. & Kirov, G. (2003) *Appl. Clay Sci.*, **22**, 295-301

Thermal transformation of chrysotile asbestos

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Chrysotile is a fibrous form of serpentine. Thermal reactions of chrysotile have been extensively investigated (see, e.g. [1]), and thermal treatment is a possible method of converting the material into less hazardous form [2].

Differential thermal (DTA) and thermogravimetric (TGA) analyses were made simultaneously on a SII NanoTechnology SSC/5200 thermal analyzer using 20 mg samples. A JEOL JEM-3200FSK instrument was used for transmission electron microscopy (TEM), scanning electron microscopy (STEM) and electron diffraction analysis. Thermal transformation of chrysotile from Thetford Mines-Black Lake, LAB Chrysotile Mine, Quebec, Canada, were heated to 1000°C in dry conditions (N_2) at a rate of 10 °/min for DTA/TG analysis was studied by TEM, STEM with EDS and selected area electron diffraction (SAED).

Morphological changes of many fibrils were observed (Fig. 1). The dehydration products have generally irregular to granular shape and a few other grains show fibrous morphology. Chemical analysis of the thermal products show intermediate compositions of forsterite and enstatite, which means that very tiny grains of enstatite were formed together with forsterite (Fig. 2). The SAED pattern is complex due to the coexistence of forsterite, enstatite, and amorphous areas.

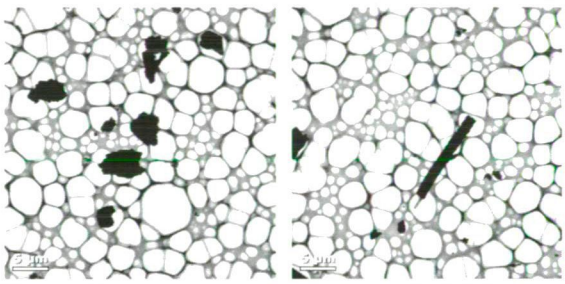

Fig. 1: TEM images of chrysotile asbestos after DTA/TG analysis. (a) granular shape grains. (b) fibrous morphology.

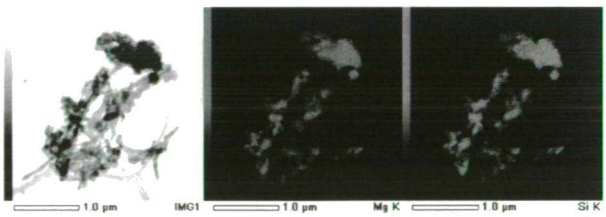

Fig. 2: STEM image (a) of chrysotile asbestos after DTA/TG analysis up 1000°C and X-ray mapping images for Mg*K*α (b) and Si*K*α (c).

[1] Souza Santos, H.D. & Yada, K. (1979) *Clay. Clay Miner.*, **27**, 161-174. [2] Gualtieri, A.F. et al. (2008) *J. Hazard. Mater.*, **152**, 563-570.

Globular phyllosilicates of the Lower Riphean Ust'-Il'ya Formation, Anabar Uplift, Northern Siberia – crystallochemical and isotope data

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Geological interpretation of K-Ar and Rb-Sr dates for globular phyllosilicates has been an important task since the 1950s, when these minerals have received wide acceptance as isotopic geochronometers. In many cases, the results agreed well with biostratigraphic data or with the ages of associated igneous rocks. But along with such data, there were overestimated or "rejuvenated" age values, and it was necessary to explain them and find criteria assuring suitability of globular phyllosilicates for dating. The structural simulation together with the Mössbauer data for globular phyllosilicates enables to estimate, whether the cation distribution in their crystal lattice is primary or resulted from post-diagenetic transformation of the mineral structure. The efficiency of such approach has been demonstrated by the examples of globular phyllosilicates of the Lower Riphean Ust'-Il'ya Formation, Anabar Uplift.

The modeling is based upon the following concept of glauconite formation. It is supposed [1,2], that an unordered distribution of the octahedral cations is typical for the newly formed glauconite. At this point atoms of the ^{40}Ar and ^{87}Sr inherited from a mineral-precursor do not leave glauconite structure yet. Only at the final stages of glauconite formation involving significant increase of the K content, the cation ordering occurs in the octahedral layer. The ordered distribution appears to result from a layer-by-layer dissolution-precipitation process. The redistribution of the cations in all glauconite layers should result in expulsion of radiogenic ^{40}Ar and ^{87}Sr alien to the mineral structure and in startup of the "radioactive clock", based on the decay of ^{40}K and ^{87}Rb. If such a glauconite is free from secondary alteration, its isotope date should correspond to the timing of early diagenesis, i.e. should be close to the stratigraphic age.

Globular phyllosilicates of the Ust'-Il'ya Formation are characterized by the ordered cation distribution in the structure formed at the stage of early diagenesis of the sediments. This means that the Ust'-Il'ya globular phyllosilicates appeared to undergo no important chemical and structural transformations which could result in loss of radiogenic ^{87}Sr and ^{40}Ar. The Rb-Sr isochron age (1483±5 Ma) and K-Ar dates (1459±10 Ma) of these minerals [3] do correspond to the Lower Riphean. An agreement between the stratigraphic position of glauconites and their isotope ages suggests that the Rb-Sr and K-Ar systems of minerals were not seriously distorted since the early diagenesis.

Acknowledgments: This study is a contribution to Programme No. 4 of the Earth Sciences Branch of the Russian Academy of Sciences. The financial support of the RFBR (grant 09-05-00877) is acknowledged.

[1] Gorokhov, I.M. et al. (1995) *Lithol. Miner. Resour.*, **30(6)**, 556-571. [2] Clauer, N. et al. (1992) *C. R. Acad. Sci. Paris, Ser. II,* **315,** 321-327. [3] Gorokhov, I. et al. (1991) *Int. Geol. Rev.*, **33(8)**, 807-821.

Response of clays on their long-term thermal treatment in open and closed systems

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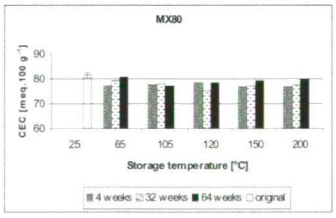
Clays are used in various applications. In many of them it is necessary to preserve their unique properties for long periods of time, e.g. in radioactive waste disposal. The presented work is focused on time dependent changes in different properties of various clays during long-term thermal treatment under near field relevant conditions. The clays under investigation are: Na-bentonite MX-80, Ca-bentonite Calcigel, Na-smectite Cloisite, vermiculite, illite and kaolinite. The clays are stored at temperatures between 50 °C and 200 °C. One group of samples is treated in an open system and the other group in closed containers with different water saturation states. Changes are expected in such parameters like cation exchange capacity and layer charge but also in related properties. Furthermore, physical parameters will be analyzed, e.g. the surface area, swelling behaviour and the thermal conductivity.

First results for MX-80, Calcigel and Cloisite show different responses on thermal treatment. The CEC of MX-80 and of Calcigel decreases during the first 4 - 32 weeks of heating. However, with longer heating the CEC gains back even at higher temperatures (Fig. 1). Cloisite, on the other hand, shows a weak but opposite tendency. The MLC of the smectites changes insignificantly and without obvious trends even after more than one year of heating.



Sample	MLC
MX80 original	0,29
Week 4_Temp. 65°C	0,28
_T105°C	0,28
_T120°C	0,28
_T150°C	0,27
_T200°C	0,27
Week 32_Temp. 65°C	0,29
_T105°C	0,28
_T120°C	0,28
_T150°C	0,28
_T200°C	0,28
Week 64_Temp. 65°C	0,28
_T105°C	0,27
_T120°C	0,27
_T150°C	0,27
_T200°C	0,27

Fig. 1: Evolution of CEC and mean layer charge of MX-80 during thermal treatment (open system).

The development of CEC cannot be explained (only) by changes in MLC. Presumably, cations in the interlayer/ ditrigonal cavities in the tetrahedral sheet are stronger bound thus preventing their exchange. Beside possible edge effects, a further process can be the formation of interlayers which are no longer accessible for the exchanging Cu-complex solution, e.g. due to occurring cementations or clay mineral transformations, i.e. formation of hydroxy-interlayered clay minerals. The evolution of water vapour adsorption is the same for all investigated clays: the adsorption ability decreases with increasing temperature but independent from heating time. XRD and FTIR investigations, the study of water uptake and swelling behaviour will give further insight to explain this phenomenon.

Thermal stability and phase transition of natural Na- and Ca-montmorillonites from China, an *in-situ* XRD study under non-ambient condition

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Two natural specimens of Na- and Ca-montmorillonite (Mnt hereafter) were collected from NW and central China [1] for physical properties research [2]. SEM and EDS analyses reveal flake-like habits of both Na- and Ca-Mnts with formulae of $K_{0.1}Na_{0.40}Ca_{0.08}(Mg_{0.54}Al_{1.44})_{1.98}(Al_{0.19}Si_{3.81})_4O_{10}(OH)_2$-$xH_2O$ and $Ca_{0.20}(Fe_{0.13}Mg_{0.72}Al_{1.40})_{2.25}(Al_{0.40}Si_{3.60})_4O_{10}(OH)_2$-$xH_2O$, respectively. The *in-situ* XRD technique was used to investigate the thermal stability and phase transition of these two typical specimens under non-ambient conditions. From room-temperature to 900°C the XRD patterns were measured at 5, 10 and 25°C intervals depending upon the gaps of phase transitions. Deconvolution technique was used to quantitatively measure the ratio of 6-water Mnt to 4-water Mnt and that of 4-water Mnt to paragonite- and margarite-like micas.

With increasing temperature from room condition to 900°C, both Na- and Ca-Mnts dehydrate and change into 9.6-9.7Å mica and finally collapse into glass. Na-Mnt dehydrates from 6-water Mnt into 4-water one in a range of 90-135°C and from 4-water Mnt into paragonite-like mica in range 175-240°C, whilst Ca-Mnt dehydrates from 6-water Mnt into 4-water one in range 40-85°C and from 4-water Mnt into margarite-like mica in 150-350°C respectively. At a little bit higher than 875°C, both paragonite- and margarite-like micas entirely collapse into black glass and yellow glass, respectively.

There exists a "step" relation between the position of "first basal reflection" of Mnts and corresponding temperature, in which there are three plateaus and two slopes. The first plateau is the stable section of 6-water Mnt, the second plateau renders that of 4-water Mnt and the third one is that of 9.6-9.7Å mica respectively, whilst the first slope indicates the transition from 6-water Mnt into 4-water one and the second slope describes the transition of 4-water Mnt into 9.6-9.7Å mica, respectively. With the help of regression analysis four equations were derived for the two slopes as:

$$d_{6/4\text{water-Na-Mnt}}(Å) = -0.461\ T(°C) + 66.77 \quad (1)$$
$$d_{4\text{water-Na-Mnt/mica}}(Å) = -0.269\ T(°C) + 64.958 \quad (2)$$
$$d_{6/4\text{water-Ca-Mnt}}(Å) = -0.197\ T(°C) + 26.259 \quad (3)$$
$$d_{4\text{water-Ca-Mnt/mica}}(Å) = -0.028\ T(°C) + 18.385 \quad (4)$$

There exist a series of correlations between the amount (integrated intensity percentage) of 6-water specimen in total Mnts, amount of 4-water specimen in the mixture of Mnt and 9.6-9.7Å mica and corresponding temperature:

$$T(°C) = 134.36 - 0.435M_{6/4\text{water-Na-Mnt}}(\%) \quad (5)$$
$$T(°C) = 83.84 - 0.477M_{6/4\text{water-Ca-Mnt}}(\%) \quad (6)$$
$$T(°C) = 239.98 - 0.661M_{4\text{water-Na-Mnt/mica}}(\%) \quad (7)$$
$$T(°C) = 153.85 - 0.384M_{4\text{water-Ca-Mnt/mica}}(\%) \quad (8)$$

Assuming that the situation of natural Mnts in air-dried condition could represent their thermal stability of formation, the Na-Mnt from NW China and the Ca-Mnt from central China would originate in a temperature range of 135-175°C and 85-150°C respectively.

[1] Xu, G.Q. et al. (1994) in Xu, G.Q. et al. (ed.) *Selected bentonite deposits in China.* Nuclear Industry Press, Beijing, 186-190. [2] Balek, V. et al. (2002) *Appl. Clay Sci.*, **21**, 295-302.

De-hydroxylation of kaolinite to metakaolin – a molecular dynamics study

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Kaolinite, $Al_4[Si_4O_{10}](OH)_8$, is a 1:1 dioctahedral phyllosilicate material and is the main component of the kaolin group of minerals. Calcining kaolinite at temperatures between 450°C and 750°C produces metakaolin – a 2-dimensionaly ordered, highly pozzolanic state that is used in the food-processing industry, oil shale processing, and ceramics and as a feedstock for geopolymer cement. The transformation is characterized by a complete de-hydration of the structure, loss of crystallinity and a concomitant change in aluminium coordination from octahedral to tetrahedral.

This transformation of kaolinite to metakaolin has been investigated using molecular dynamics (MD) simulations with an empirical force field that accurately produces the experimental kaolinite structure. Starting from the kaolinite structure (Fig. 1) we performed a series of NPT runs with increasing levels of de-hydroxylation to understand the effects on the structure of kaolinite and the change in aluminium coordination. Our study shows, for the first time, the atomic mechanisms underpinning the loss of crystallinity, which occurs during the de-hydroxylation of kaolin to metakaolin (Fig. 2).

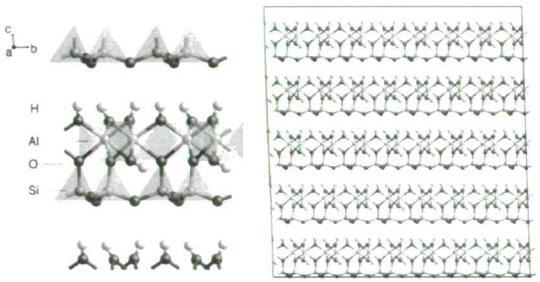

Fig. 1: Layered structure of kaolinite (left) and the initial simulation cell prior to de-hydroxylation (right).

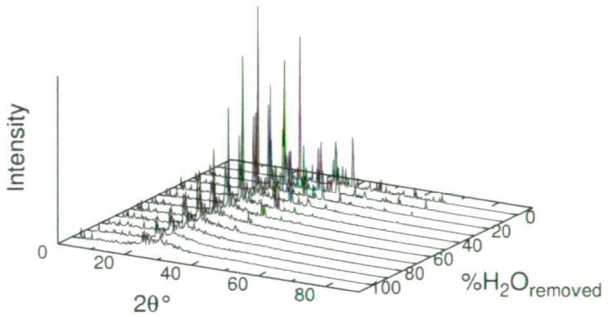

Fig. 2: Simulated x-ray diffraction data showing the loss of crystallinity.

Intercalation and dynamics of hydrated Fe^{2+} in the vermiculites from Santa Olalla and Ojén (Spain)

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Whereas the uptake of Fe^{3+} into vermiculites and smectites via ion exchange is notoriously difficult and accompanied by the deposition of iron oxyhydroxides on the external surfaces of the phyllosilicate particles [1], the insertion of Fe^{2+} is much easier. To reduce the tendency towards oxidation one can carry out the ion exchange under nitrogen or one can use Fe^{2+} salts (e.g. gluconate) which are less sensitive to oxygen. The vermiculites were treated twice for one hour with freshly prepared Fe^{2+} solutions. Afterwards the solid was washed at least five times with deaerated water and dried. The samples so obtained were stable against oxidation for months when stored in closed vessels (no special protection against air).

The Mössbauer spectrum at room temperature (Fig. 1) looks like the typical spectrum of a vermiculite. Just the peak at ~2.5 mm/s belonging to the quadrupole doublet of the Fe^{2+} site gets slightly broader towards higher quadrupole splitting and increases in intensity slightly.

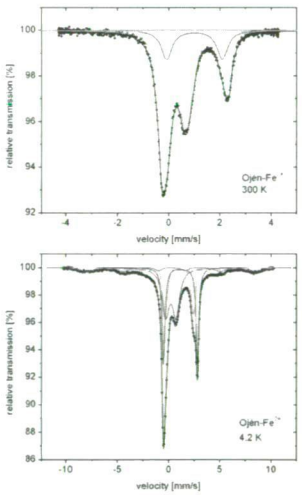

Fig. 1: Mössbauer spectra of the Fe^{2+} intercalated Ojén vermiculite at room temperature (top) and at 4 K (bottom). Dots are the data points, the solid lines marks the individual components as obtained from the fit to the data points.

At 4 K the right of the peak at 2.5 mm/s (Fig. 1) increases dramatically in intensity and the quadrupole splitting of this new site (~3.3 mm/s) can be assigned to the hydrated Fe2+ ions. The dramatic increase in intensity as a function of temperature is mainly due to a strong rise of the Mössbauer-Lamb factor at low temperature, indicating that the Fe2+ ions, which are highly mobile at room temperature, are frozen in definite lattice sites at low temperature. We will discuss also the temperature dependence of the rise of the Mössbauer-Lamb factor with increasing temperature.

[1] Ramírez-Valle, V. et al. (2008) *Clay Miner.*, **43**, 487-499.

High-pressure phase transitions in serpentines

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Serpentines are formed by interaction of water with basic to ultrabasic rocks under conditions that range from shallow (<10 km) ocean floor hydrothermal systems to intermediate depths (150-200 km) of subduction zones. Several Raman and X-ray diffraction data on various serpentine varieties at pressures up to 10 GPa [1-3] suggested phase transformations that were recently confirmed by single-crystal X-ray diffraction on antigorite [4]. DFT calculations on lizardite [5] suggested phase transformation at higher pressures.

We performed first-principles calculations on lizardite using the generalized gradient approximation (GGA) of the density functional theory as implemented in the ABINIT package based on plane waves and pseudopotentials. We compute the lattice dynamical properties, the phonon frequencies and the atomic displacement pattern of the vibrational modes within the density functional perturbation theory.

Results of DFT calculations are compared with former and new high-pressure Raman spectroscopic data and with X-ray diffraction data. They show good agreement on phase transitions observed below 10 GPa. Consequences for serpentine seismic properties and detection in subduction zones are discussed.

[1] Auzende, A.L. et al. (2004) *Phys. Chem. Mineral.*, **31**, 269-277. [2] Hilairet, N. et al. (2006a) *Geophys. Res. Lett.*, **33**, L02302. [3] Hilairet. N. et al. (2006b) *Phys. Chem. Mineral.*, **33**, 629-637. [4] Nestola, F. et al. (2010) *Contrib. Mineral. Petrol.*, **60(1)**, 33-43. [5] Mookherjee. M. & Stixrude, L. (2009) *Earth Planet. Sci. Lett.*, **279**, 11-19.

High-pressure transformations in kaolinite

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Polytypic transformations are a key aspect of the crystallography and stability of sheet silicates. However, their physical significance in natural systems at high P is largely unexplored.

Kaolinite, $Al_2Si_2O_5(OH)_4$, is a hydrous sheet-silicate of considerable geological, industrial and technological importance. While numerous studies of its ambient and near-ambient stability and geochemistry have been made, almost nothing is known about its P response. Recent modelling of kaolinite stability by *ab initio* methods [1,2] has predicted a sequence of polytype stability as a function of P: kaolinite ("kaolinite-I", polytype 1Ia of [1])→ "kaolinite -II" (polytype 5a or 7a of [1])→ "kaolinite -III" (polytype 18 of [2]). Unlike kaolinites I and II, kaolinite–III has trifurcated interlayer H-bonds that arise from the operation of an unusual layer stacking vector and the production of a new kind of polytype.

We have studied the behaviour of Keokuk kaolinite (space group $C1$) to 8 GPa at 298 K using synchrotron X-ray powder diffraction and a diamond-anvil cell [3]. Two transformations were encountered: kaolinite-I → kaolinite -II at 3.7 GPa and kaolinite-II → kaolinite -III at 7 GPa. The two high-P phases were identified from calculated diffraction patterns based on the model polytype structures listed by [1,2]: kaolinite-II is the 5a polytype of [1], and kaolinite-III is the one-layer model 18 polytype of [2]. Thus, experiment has confirmed the predictions of *ab initio* modelling.

Both transformations involve layer translation without rotation. Kaolinite I↦II involves the removal of unfavourable vertical cross-interlayer Al-Si superpositions, and so is analogous to the 2.7 GPa transformation in dickite [4]. Kaolinite II→III involves the formation of a new kind of polytype, which has a very different hydrogen-bonding topology and layer stacking from kaolinites I and II. Kaolinite-III can be quenched to ambient conditions from 7.8 GPa. Its ambient density of 2.77 g/cm^3 is 6% higher than those of kaolinite-I, dickite and nacrite; thus, it is a significantly collapsed structure.

Bulk and linear moduli for kaolinites I and III were obtained from compression curves of the EoS study. Unit-cell parameters were obtained by refinement of powder diffraction patterns and fitted to a 2nd-order Birch-Murnaghan EoS ($K' = 4$).

Kaolinite-I: K_0 = 59.7(0.7)GPa, K_a = 88.6(3.5)GPa, K_b = 85.4(2.8)GPa, K_{001} = 34.6(0.5)GPa.

Kaolinite-III: K_0 = 50.2(1.5)GPa, K_a = 63.3(4.1)GPa, K_b = 54.8(1.6)GPa, K_{001} = 38.2(1.2)GPa.

The higher compressibility (lower K_0) of kaolinite-III is due to softening parallel to the polyhedral sheets.

[1] Mercier, P.H.J. & Le Page, Y. (2008) *Acta Cryst.*, **B64**, 131-143. [2] Mercier, P.H.J. & Le Page, Y. (2009) *Mat. Sci. Tech.*, **25**, 437-442. [3] Welch, M.D. & Crichton, W.A. (2010) *Am. Mineral.*, **95**, 651-654. [4] Dera, P. et al. (2003) *Am. Mineral.*, **88**, 1428-1435.

Trioctahedral micas: relationships between crystal chemistry and magnetic behaviour

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This study is aimed at verifying the factors affecting magnetic susceptibility χ variation in micas in relation to: I) Fe content; ii) Fe^{2+}/Fe^{3+} ratio; iii) occurrence of Fe in tetrahedral and octahedral sites, outlining possible ordering effects.

Other aspects considered in our study will involve: i) eventually observed variation in magnetic properties for samples showing similar chemical composition, but occurring from different areas and different crystallization environments; ii) possible influence of strong magnetic anomalies over magnetic properties of samples therein occurring.

All these aspects were thus addressed by characterizing samples belonging to phlogopite – annite, tetra-ferri-phlogopite – tetra-ferri-annite and polylithionite – siderophyllite series. Some samples, representative of the whole sample set, were then selected for magnetic susceptibility characterization. Some of them also required calorimetric analyses, in order to better describe and understand their behaviour.

Other experimental methods used in this investigation include: electron microprobe, structure resolution by X-ray single crystal methods, X-ray absorption spectroscopy, with a particular attention to the understanding of the XANES region.

Main results demonstrate that: i) magnetic phenomena associated with maxima of magnetic susceptibility could be observed at low temperature (T<10 K) and weak magnetic field (10 Oe); ii) magnetic properties depend not only on the total Fe content. Samples where Fe is mostly in octahedral coordination are predominantly ferromagnetic, strongly depending on the $[6]Fe^{2+}/([6]Fe^{2+}+[6]Fe^{3+})$ ratio, which was observed to increase with Curie-Weiss θ constant (ranging from 13 to 24 K and from 4.4 and 5.2 K for samples showing higher and lower $[6]Fe^{2+}/([6]Fe^{2+}+[6]Fe^{3+})$ ratio, respectively). In tetra-ferri-phlogopite, dominant interactions were observed to be anti-ferromagnetic, as shown by a negative Curie-Weiss θ constant value (-25 K). Furthermore Curie-Weiss constant (θ) and the temperature value giving the maximum in the magnetic susceptibility (Tm) seem to be dependent not only on the mean number of Fe atoms in octahedral coordination (Z) per unit cell, but also on its ordering. Tm linearly depends on several structural parameters as well, e.g., the tetrahedral rotation angle α.

Effect of temperature on Hg-cysteine complexes in vermiculite and montmorillonite

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This work describes the influence of temperature on two Hg(II)-cysteine modified clay minerals with different layer charge (*i.e.*, vermiculite and montmorillonite) by using chemical analyses, thermal analyses coupled with evolved gas mass spectrometry (TGA-MSEGA), synchrotron-based X-ray absorption spectroscopy (XAS), and X-ray powder diffraction (XRPD) techniques. These two latter techniques were applied on samples heated "*in situ*" up to 900°C. Hg binds cysteine by the thiol group with Hg–SH bond lengths similar in both clay minerals, thus suggesting their independence from layer charge. On the contrary, the thermal behaviour of the adsorbed organometallic complexes is strictly layer charge dependent, as evidenced by decomposition temperatures, which are commonly lower in montmorillonite than in vermiculite. Results from X-ray absorption near edge structure (XANES) spectroscopy evidence a nearly completely Hg removal in montmorillonite at temperature values ranging from 600 to 700°C, unlike in vermiculite where Hg is still present at these temperatures.

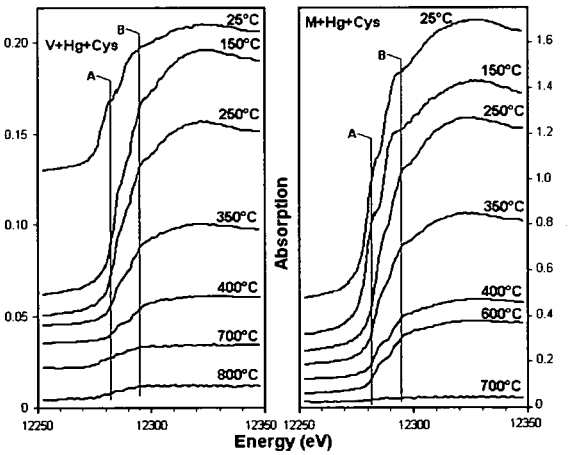

Fig. 1: XANES spectra of Hg-Cysteine treated vermiculite (left side) and montmorillonite (right side) vs. temperature.

Kinetics of Zn-Al hydrotalcite structure reconstruction process

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The unique ability of anionic clays known as „memory effect" allows for the reconstruction of the layered structure of calcined hydrotalcite-like samples. In view of this, our intention was to investigate the kinetics of structure reconstruction of the zinc-aluminum hydrotalcite type samples calcined at 450 °C for 3 hours. Hydrotalcite-like samples (Htl) with atomic ratio of Zn:Al = 3:1, synthesized by standard co-precipitation method at a constant pH=7, using either Na_2CO_3 and NaOH, or $(NH_4)_2CO_3$ and NH_3 (aq) for precipitation and control of pH. The precipitates were calcined at a desired temperature and subsequently exposed to humid air at room temperature.

XRD analysis of the starting materials confirmed that the synthesized samples possessed Htl structure, mainly with carbonates as compensating anions. The presence of some nitrate anions was evidenced with the EGA and FTIR results. Nitrate contribution was, at least in part, associated with $Zn_3(OH)_4(NO_3)_2$ phase whose traces were observed in both samples (especially in the solid synthesized with Na_2CO_3 and NaOH). XRD patterns of calcined samples showed strongly amorphous materials, with poorly crystalline ZnO as the only identifiable phase. The reconstruction process was carried out at controlled humidity (94%) and temperature (295K) conditions.

Already after 10 days in all calcined samples strong reflections originating from recovered Htl structure were observed. The progress of reconstruction was investigated over a period of up to 150 days. In all samples, independently of the applied preparation method, the position of d_{003} reflection was constant and appeared at 0.755 nm, which shows that, as expected, a carbonate form of Htl was formed upon reconstruction. Even after the longest applied treatment (150 days), not all of the ZnO phase was consumed. Analysis of the XRD patterns suggests that in the first place reconstruction occurs at the expense of the finest ZnO grains. Apparently, their high surface energy is responsible for facile rebuilding of the Htl lattice at the beginning of experiment.

Noteworthy, crystallinity of the reconstructed phase was better than that of the starting Htl. This is also illustrated by SEM images, which show the changes in grain morphology at different stages of the reconstruction experiment.

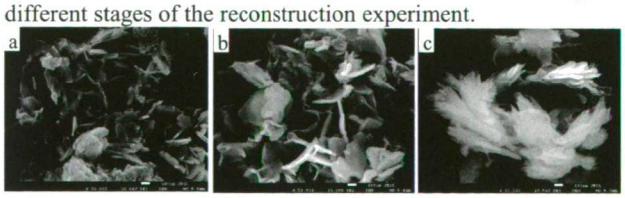

Fig. 1: SEM images of a) fresh Zn-Al Htl precipitated with Na_2CO_3 and NaOH, b) calcined at 450°C, c) after the reconstruction.

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Deformation and lattice preferred orientations of antigorite serpentine

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Antigorite is the major component of serpentinites in subduction zone context. Its presence and deformability likely control the downdip extent of the seismogenic zone and exhumation processes. Lattice preferred orientations (LPO) of serpentines induce a strong anisotropy of various properties in serpentine bearing-rocks. For example, seismic anisotropy is potentially extreme in serpentinites and may allow their seismic detection as well as the determination of the deformation pattern at the plate interface and in the mantle wedge. LPO of antigorite had so far been obtained only by X-ray diffraction techniques. We have applied EBSD to the measurement of the LPO of antigorite in a naturally deformed high-pressure serpentinite. This technique is very sensitive to sample preparation that can lead to surface amorphization in the case of serpentine. A polishing procedure is described that avoids amorphization and allows accurate EBSD measurements with optimized experimental conditions in a variable pressure SEM. Results indicates that deformation leads to LPO characterized by extremely strong c-axis clustering perpendicular to the foliation, as expected for a layered silicate. In the foliation plane, a significant clustering of the a-axis is observed and tentatively attributed to intracrystalline deformation mechanisms. These data suggest that antigorite deforms mostly by gliding along the basal plane of the layered phyllosilicate structure, but that gliding may occur along directions favoring a-axis alignment. EBSD appears to be a reliable method for determining phyllosilicate LPO in deformed rocks, with potential applications for determining anisotropy of properties like seismic velocities or thermal and electrical conductivities. Applications concerning seismic anisotropy are shown. Comparison with deformation in experimentally deformed antigorite is in progress and will be presented.

Influence of clay microfabrics on petrophysical properties of clay stones and bentonites

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Claystones and bentonites are currently being investigated as potential host rock and geotechnical barrier, respectively, for radioactive waste disposal. For this application, the hydraulic conductivity, swelling properties, water uptake, rheological and mechanical properties are important. The Opalinus Clay (Mont-Terri, Switzerland) and the Callovo-Oxfordian clay stone (France) are the most frequently studied clay stones. One goal is to develop a numerical model being able to predict the mechanical behaviour of clay stones under repository-like conditions.

The results of this study show that Opalinus Clay and Callovo-Oxfordian clay stone behave different with respect to the dependence of mechanical strengths on the carbonate content. The failure strength of Opalinus Clay decreases with increasing carbonate content, while it increases for Callovo-Oxfordian clay stone [1]. For the investigation of the microfabrics, scanning electron microscopy of polished sections and image analysis were used. Opalinus Clay shows large elongated carbonate grains of shell fragments, whereas Callovo-Oxfordium clay stones show a homogeneous distribution of fine-grained and more isometric carbonates. The most important result of this study is that not only the carbonate content, but also the microstructure (grain size distribution, shape, spatial distribution, and intergrowth of carbonates) affects the mechanical behaviour of the claystones. The microscopy and image analysis techniques proved to be an excellent tool, which can be employed in model development.

Furthermore, the microfabric of 38 bentonites was investigated. During genesis bentonites undergo continuous maturation from glass to smectite. Almost all bentonites show glass relict structures. The microfabric of the bentonites, particularly the intergrowth with relict volcanic glass may have an additional influence on relevant geotechnical properties. Based on the optical characterisation, a model of maturation was developed, containing five alteration-classes. The following petrophysical properties of bentonites were determined and compared to the microstructural characteristics namely density, porosity, BET-surfaces, abrasivity of bentonite suspensions [2], electrical conductivity, and water uptake capacity [3]. The results show that all these properties are affected by the microfabric.

[1] Klinkenberg, M. et al. (2009) *Eng. Geol.*, **107**, 42-54. [2] Klinkenberg, M. et al. (2009) *Appl. Clay Sci.*, **46**, 37-42. [3] Kaufhold, S. et al. (2010) *Clay Clay Miner.*, **58(1)**, 37-43.

Relationship between morphological preferred orientations and landslides

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Crystals orientation in polycrystalline natural compounds may be either completely random or else follow preferred directions, which reflect physical processes in which the materials have been involved during the solidification and / or after the solid state had been reached.

The preferred orientation can be divided into two main groups: i) preferred orientation of the crystal lattice (LPO, lattice preferred orientation) and ii) grains preferred orientation (i.e., morphological preferred orientations, MPO). Frequently there is a close relationship between these two groups. Geological processes that determine the formation of LPO are, for example, tectonic (regional) compressive movements; on the other hand MPO can be induced also by local stress (i.e., gravitational movements). While tectonic (regional) compressive movements may produce LPO even on already lithified rocks, usually, MPO are induced only on not-lithified and incoherent rocks.

The preferred orientation cab be observed: i) macroscopically (the rock structures) ii) microscopically, grains orientation and morphological textures of the rock according to the classic concept of optical microscopy, iii) with diffraction methods (i.e., X-rays and neutrons diffraction), to study both LPO and MPO when, this last, cannot be studied via optical methods because, for example, of a very small grain size.

This research will investigate MPO via X-ray diffraction only. We collected, and kept oriented, samples in several landslide areas. In particular samples were collected both in the active crumbling area and at the landslide margin. Samples were analyzed for texture using X-ray diffractometer equipped with a phi-chi Eulerian cradle. We analyzed the preferred orientation of the hkl reflections: i) (001) and (060) in smectiti and illite; ii) (001) and (100) in caolinite; iii) (24-1) in plagioclase.

Preliminary investigation demonstrated a direct correlation between the number of MPO and the amount of clay minerals. Texture measurements on samples collected in the crumbling area agree with other morphological field measurements, providing, in addition to the main direction of the landslide, also the vertical module, thus probably defining the preferential path for interstitial fluids migration. Only in one case we could observe preferred orientation in a sample coming from a margin of a landslide, data which could testify a past movement (paleo-landslide) or else a quiescent landslide.

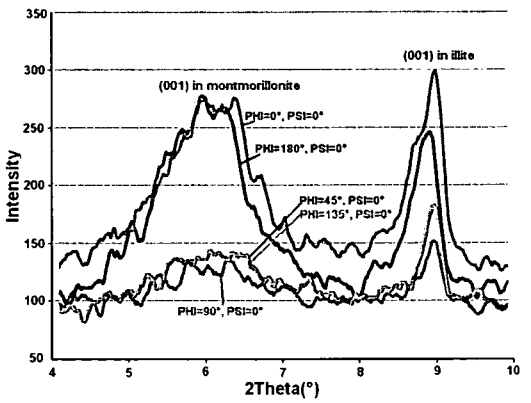

Fig. 1: Intensity variation of (001) in montmorillonite and illite varying sample orientation.

The influence of scaly fabric on the illitization reaction in faulted claystones

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A closely-spaced fabric, related to the interlacing of striated and polished shear planes, is commonly defined as scaly fabric in the geological literature. A tens-of-meters-wide belt characterized by pervasive scaly fabric occurs in claystones of the Northern Apennines foothills, south of the town of Bologna, in a shallow-level fault zone. The shear planes are arranged in different oriented sets defined hereafter as R, P, R' and D planes, following the terminology after Tchalenko (1968) [1].

Microscopical observations (SEM) show a significant increase of parallel orientation of the clay platelets ("face to face" arrangement) on the surfaces and in the proximity of shear planes, leading to development of clavage domains and porosity decrease. Despite, far from the shear planes in the undeformed domains (microlithons), the clay particles show a more open texture with a "edge to face" disposition, due to a more disordered arrangement of the clay particles.

A systematic mineralogical study performed by XRD on the less than 2 micron grain-size fraction has evidenced a progressive illitization of smectites and mixed layer illite/smectites (I/S) along shear planes and cleavage domain associated. The progressive change from smectites-rich I/S into illite-rich I/S was also confirmed by microchemical EDS data, which showed an enrichment in K^+.

The studied claystones were sampled in absence of significant mechanical compaction and clay mineral diagenesis and the alignment of clay platelets and illitization occurred in shallow burial conditions and very low thermal maturity (< 60°C) [2]. Moreover, the illitization reaction in the scaly cleavage domain is isothermal and probably driven only by K^+-rich fluid circulation.

The progressive transition from smectite-rich I/S to illite-rich I/S is due to enhanced fluid migration, which is preferred within the scaly cleavage domains because enriched in oriented phyllosilicates (P-domains), whereas the circulation is inhibited in microlithon cores because of disordered arrangement of clay particles. The anisotropic fabric is caused by tectonic strain, which produces flattening and extension of clayey rocks leading to a volume decrease and consequent fluid expulsion. This tectonic dewatering mechanism involves chemical changes within the microstructural domains favouring progressive illitization of clay particles.

[1] Tchalencko, J.S. (1968) *Tectonophysics*, **6**, 159-174. [2] Dellisanti, F. et al. (2008) *Int. J. Earth Sci.*, **97**, 601-616 .

Experimental shear test of montmorillonite: the role of water on geomechanical behaviour of smectite

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In order to investigate the role of the interlayer water molecule of Ca-montmorillonite on the geomechanical behaviour, a cycle of controlled experimental shear deformations on natural and structurally modified Ca-montmorillonites have been performed and correlated to structural and morphological analysis. Experimental shear tests were performed on five types samples: (1) a natural Ca-montmorillonite; (2) the same montmorillonite after heating for three hours at 80°C; (3) at 250°C; (4) at 335°C, and (5) after inducing defects in the tetrahedral and octahedral sheets. The five samples have been shear-tested by a specifically built shear box apparatus under 19.6 MPa condition of normal pressure. All samples, before and after the shear deformation, have been analysed by SEM and XRD.

The shear-deformed samples were cohesive and presented striated and polished shear planes along the displacement surfaces imposed by the experimental apparatus. The shear planes were arranged in sets disposed at low angle with respect to the principal shear surface, which correspond to R, P and D planes, [1,2]. The disposition of planes and the lustrous aspect of the surfaces are quite similar to the ones observed in natural examples. In our experiments striations are not related to ploughing by coarse grains or asperities because we have deliberately used montmorillonite with homogeneous composition and granulometry. XRD and SEM analyses indicated that in the vicinity of the shear planes the clay platelets appear preferentially orientated and with a "face to face" arrangement, whereas in zones far from the shear planes the platelets present a lower degree of orientation and an "edge-face" disposition. The shear strain also produced a reduction of structural ordering and an increase of both lattice defects and microstrain in the mineral. Moreover, natural montmorillonite presented a typical strain softening behaviour and the geotechnical parameters (cohesion and internal friction angle) of overconsolidated clayey rocks

The cohesion and compaction of the material are essentially related to the capability to release what is called "absorption water", whereas the development of striated shear planes has to be attributed to the role of interlayer water. The last hypothesis is supported from the experiments carried on the same material heated up to 80°C (to desorb completely the water), which showed only scaly cleavage and striations. Samples heated up to 250 and 335°C, which have almost completely lost the interlayer water molecules, did not show neither development of scaly cleavage nor striations on the principal shear surface. However, they showed a very moderate strain hardening behaviour. Defective montmorillonite with disorder in the tetrahedral and octahedral sheets (hindering absorption and release of water, as described by [3], presented, as expected, a strain hardening behaviour without any striations and scaly cleavage. The general strain softening behaviour of natural montmorillonite can be explained by the presence both absorption and interlayer water that allow the sliding of clay platelets along the TOT layers. However, the montmorillonite, which contains defects and disorder is hindered to a deformation by a sliding mechanism and therefore does not develop shear planes and alignment of clay platelets.

[1] Skempton, A.W. (1966) Proc. *Int. Soc. Rock Mechanics Congress*, **6**, 329-335. [2] Tchalencko, J.S. (1968). *Tectonophysics*, **6**, 159-174. [3] Dellisanti, F. & Valdrè, G. (2005) *Appl. Clay Sci.*, **28**, 233-244.

Adsorption properties of clays in teaching of Environmental Chemistry

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In the last fifty years, environmental issues has required the study of air pollution, water and soil to prevent and remedy the adverse effects of waste originating from anthropogenic activity and the development of new energies and new materials. The teaching of this discipline has been marked by lectures on general lines, materials, disciplines, who explained biased objects of reality, but often forgot the task of reconstruction and integration of such visions. Moving from that model, otherwise quite static, to a dynamic relational model, would in our view, a real revolution in education. This means taking a systematic approach to complex both in interpreting reality and in favor when learning. Children relationships are as important or more than single objects, and it is to discover fundamental organizational principles of phenomena we seek to interpret or in other words, find the pattern that connects. Thus, we must work on relationships and also take into account the relation between the observer and the observed. Educate about relationships means that studies should always be considered within a framework of probabilities, not absolute certainties.

This model of systemic thinking, dealing with complexity, is a possibility to bring coherence to our educational work, because the complexity is not taught, complexity is live, so that complex thinking is extended (and fed) in a form educate complex. It is the task of teaching to help people move from level to level of decision reviews. This means that systems thinking should be extended in a local action, action that engages the individual and the environment. So we must work with our students helping them to understand, in this case, environmental problems from their daily reality, where the real subject of study.

Environmental Chemistry has emerged as a discipline of free choice for pupils attending chemical engineering which has been assigned 4.5 credits theorists. The chemical engineer's professional profile within the current framework is defined as a professional knowledge as a specialization technical / functional, working in a learning organization and the formation of which enables him to continuous improvement and innovation.

There are different materials used in the adsorption and immobilization of chemical contaminants, most of which remain under patent, so they do not know the procedures and products used, but in all cases the safety and / or biodegradability of materials used is an important issue in their choice for environmental applications. Regarding the materials, safe and low cost, clays and clay minerals must be mentioned, because their colloidal properties, ease of generating structural changes, abundance in nature and low cost make them very suitable for absorption of chemical contaminants. We proposed to use these materials to show the different aspects for the study of the Enviromental Chemistry.

Minerals in context: the Earth, rocks, and society

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Minerals are the fundamental building block of our Planet and are the heart of a geoscience education. Yet, there is an increasing perception that a foundation in mineral sciences is no longer relevant, nor critically necessary for a comprehensive geosciences education. Teaching *"minerals in context"* provides a powerful approach for engaging students in the exciting, important and socially relevant field of mineralogy.

At Louisiana State University, U.S.A., this is accomplished in three different classes ranging from the required mineralogy course through elective advanced courses. For our first core curriculum course in mineralogy, the context of minerals is Planet Earth and the approach focuses on teaching minerals from the core to the crust. Systematic mineralogy is introduced via elements in the core and proceeds outward increasing in mineral complexity as one proceeds to the crust. With this emphasis, crystallographic concepts are woven into the discussion of minerals as they are encountered. For example, mantle minerals provide a backdrop for teaching polymorphic phase transitions in context of their environment in the transition zone. Further, relevance can be given by connecting to deep-focus earthquakes. Crystal chemical concepts are reiterated once crustal minerals are described. This approach sets the stage for the multitude of complexity found in crustal minerals both in terms of environment, chemistry, and structure. Here, numerous connections are made with reference to minerals in our lives as well as minerals as key indicators of environmental conditions. Such an approach emphasizes the central focus of mineralogy and its linkage to other disciplines.

For the advanced level, two approaches continue to focus on teaching minerals in context: minerals as fingerprints of geologic conditions (in the course Petrologic Mineralogy) and minerals in our lives (course: Earth Materials and the Environment-EME). Petrologic mineralogy continues to explore the crystal chemistry and structure of minerals in the context of deciphering tectonic evolution; that is, minerals as geochronometers, geothermobarometers and/or as provenance indicators. In this course, students complete a semester-long research project where they chemically analyze minerals in order to determine derivative information such as P-T, age, or source. In contrast, for the EME course, minerals are explored as both problems and solutions in the context of societally relevant issues. These range from various health effects (e.g. asbestosis, silicosis), to solutions for global warming (e.g. carbon capture and sequestration) and nuclear waste (e.g. material templates for encasement, geologic barriers), to requirements for our standard of living (e.g. metals, rare earth elements, PGEs). Such a context not only raises awareness of the critical nature of our science and its importance to government policy but also provides opportunities for improving critical thinking skills as related to the development of public policy dealing with these issues. In both cases, students appear to engage more fully in the material because it relates to their lives and opens their eyes to potential career goals.and their everyday lives.

Volcanic petrology in six weeks

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At the University of Calgary students have to learn igneous petrology in six weeks. I've heard of similar reductions in time allocated to mineralogical science courses at other universities. Responses to the reductions included: provide an overview, teach everything anyway, or teach through special projects. An overview provides little depth. Covering everything leaves students frustrated and feeling inadequate. Projects are great but students don't reach an appreciation of the many different faces of igneous petrology.

Several decades ago, the goal of a geology program was a student who could work at a professional level in any geologic setting. Today, many students specialize; they expect to work at the professional level in the energy industry, on problems of climate change, or on problems of environmental remediation, to name but a few popular career fields. Prospective employers often share their expectations. Most students graduating with geoscience degrees will never look at an igneous rock as a professional geoscientist. Why then, do they need to learn about igneous rocks? This is the first of three important questions that geoscience educators must answer if they expect to keep igneous petrology in geoscience curricula.

Igneous petrology is integral to geoscience. Igneous events sporadically intrude themselves into our lives, often with a vengence. Those who graduate with a degree in geoscience will be expected to assess the events for themselves, their families, and their communities. If they cannot, their reputations will suffer along with the reputations of the departments granting their degrees and along with the reputations of the faculty in those departments.

Second question: supposing these arguments convince the powers that be to keep igneous petrology in the curriculum, what should be included in a six-week course? At a minimum, geoscience graduates should be able to assess articles on igneous phenomena in popular science magazines such as *National Geographic*, *Scientific American*, *American Scientist*, *Elements*, and *Earth*. I recently reviewed several issues of these magazines and compared their contents to the material I had taught in igneous petrology a decade ago. Two features stood out: (1) Articles were almost always about volcanic, not plutonic, events and products; (2) The articles were devoid of rock names, textural descriptions, rock compositions, and theoretical petrology, for example thermodynamics and phase diagrams. The articles focused on the effects eruptions had or could have on society and civilization. I would leave out plutonic rocks and theoretical petrology. Six weeks is not enough time to do justice to all three aspects. Geologic context, texture, mafic index, silica activity, alumina activity, and chemical composition would be emphasized. If students know something about these features for any particular volcanic rock they will know a lot about its nature and can infer much about the processes that formed it.

Third question: how can a six-week course in volcanic petrology enhance the degree of an undergraduate who plans a specialized professional career?

Graduating students should be able to discover the geologic context of a volcanic rock, describe its textural features, identify the critical minerals it contains, and become familiar with its chemistry. With this background, they should be able to read and assess mass media accounts of volcanic activity, take part in geoscience outreach programs where they could talk about volcanic phenomena with confidence and without misconceptions, and they should be able to write accounts of volcanic phenomena suitable for popular science magazines.

Teaching mineralogy for geology students at the Eötvös L. University, Budapest, Hungary

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Teaching mineralogy at the Eötvös L. University began in 1774. The separate Department of Mineralogy was established in 1849. From this time several text-books were available based on Dana's Mineralogy or Klockmann and Ramdhor text-books. After World War II., geology training started and students of geology received detailed and specialised mineralogy during the first and second semester. Due to the demand of students of geology several university notebooks and textbooks were published. The last one was the textbook of Koch S and Sztrókay K. I (first published 1955, last one in 1986 in two volumes). These lectures and text-books, besides the well known general mineralogy (crystallography, X-ray crystallography, crystal chemistry, physical properties of minerals etc.), dealt with systematic mineralogy. The systematic mineralogy part, written by Sztrókay, differs from the previous text-books. It is based on crystal chemistry and the sequence of mineral classes reflects Sztrókay's concept [1].

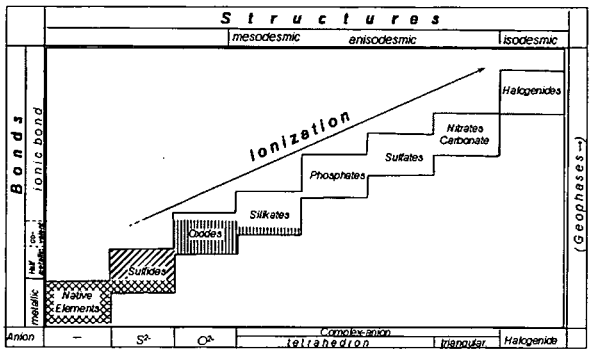

Fig. 1: Sequence of mineral classes by K. Sztrókay (1982).

He started with metallic (native metals and sulphides), followed by covalent (oxides) and more and more ionic bonds (silicates, phosphates, sulphates, borates, carbonates, nitrates, halogenides) and finished with the molecular structures of organic minerals. When describing the individual mineral species, Sztrókay included crystal structure, lattice parameters etc., but also emphasized the diagnostic features and gave information on genetics and localities needed for geologists. Unfortunately the two levels (BSc, MSc) of the new Bologna-system radically decreased number of the lectures of mineralogy. Basic knowledge of natural sciences by secondary school students is becoming poor and consequently there is now little chance to make them understand principles of mineralogy. There is a greater chance that mineralogy as one of the main subjects for students of geology shall disappear from the geology curriculum in Hungary.

[1] Sztrókay, K.I. (1962) *Über die Grundprinzipien einer zeitemässen Systematik des Mineralreichs*. I. Teil. Ann. Univ. Scien. Bp. de R. Eötvös Nom. Sec. Geol. Budapest, **5**, 139-149.

Teaching of crystallography and gemmology at the "Museum of Unique Crystals", Sofia, Bulgaria

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The newest mineralogical museum in Bulgaria is devoted to the famous collector and donator of Bulgarian origin – Mr. Ilia Deleff, who in the past decades worked for preservation of the mineral heritage on the planet. Mr. Deleff (Brazilian citizen, born 1921 in Bulgaria) is a well known collector of phenomenal giant and rare minerals. In 1983 Mr. Deleff exhibited for the first time in the world his collection with giant crystals in the National Museum of Natural History in Paris. In 1987 in Sofia was opened to the public the "Earth and Man" National Museum, where the main and central part constitutes the remarkable collection of Mr. Deleff of unique giant quartz crystals and other minerals from Brazil [1]. In Bulgaria Mr. Deleff made also several donations with minerals from Brazil to the University of Mining and Geology "St. Ivan Rilski" in Sofia, which can be seen in the newest mineralogical museum – Museum of Unique Crystals "Ilia Deleff". In the museum are exhibited rare crystals and minerals from Brazil in the following sections: crystal flowers of nature; parade of phenomenal crystals; treasures of Minas Gerais; gem pegmatite minerals; mineral wealth of Brazil; world of agates; the noble amethyst; the quartz palette; rock crystal fairy; nature and art. Special ascents at the museum are the "Amethyst Room" and the "Rock Crystal Cave".

The Museum of Unique Crystals (MUC) at the Rectorate is open to the public and for social events as the most representative museum among the other academic museums (geological and paleontological; mineralogical and petrographical) at the university. Since its opening in November 2007 the MUC serves also as a place for lectures and education in mineralogy and crystallography for the bachelor degree [2] and in gemmology for the bachelor and master degrees [3]. Impact in the teaching process is made on the richness of crystal habits of minerals [4], mainly quartz varieties of different size, perfection and colour, as well as some gem minerals as topaz, beryl, tourmaline, kunzite and feldspar. As Bulgaria is not so rich of gem and decorative minerals [5] compared to Brazil, the exhibit allows a broad enrichment of the knowledge of different common and rare mineral species. The main hall is used for presentations and scientific films, including for scientific conferences. Students and other visitors of the museum are assisted in their mineralogical research also by a gem and mineral shop.

[1] Deleff, I. (2004) *Phenomenal Crystals*. Pensoft, Sofia-Moscow. [2] Kostov, R.I. (2000) *Fundamentals of Mineralogy*. Pensoft, Sofia-Moscow (in Bulgarian). [3] Kostov, R.I. (2003) *Precious Minerals: Testing, Distribution, Cutting, History and Application (Gemmology)*. Pensoft, Sofia-Moscow (in Bulgarian). [4] Kostov, I. & Kostov, R.I. (1999) *Crystal Habits of Minerals*. Bulgarian Academic Monographs, 1. Co-published by Pensoft Publishers and Prof. Marin Drinov Academic Publishing House, Sofia. [5] Petrussenko, S.I. & Kostov, R.I. (1992) *The Precious and Decorative Minerals in Bulgaria*. Publishing House of the Bulgarian Academy of Sciences, Sofia (in Bulgarian with a Russian and English abstract)

Interactive Wolfram Mathematica demonstrations and physical models for studying crystal structures

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From Version 6 on (launched on May 1, 2007) the computer software Wolfram Mathematica is capable of showing interactive graphics, which can be used preferably to study crystal shapes and structures. In this paper selected demonstrations are shown that are related to crystal structures (Fig. 1-3). In the last part the modeling with polystyrene blocks is introduced. The blocks are cut out with the proprietary machine of the author, and then sticked together (Fig. 4) (http://demonstrations.wolfram.com/search.html?query=kabai).

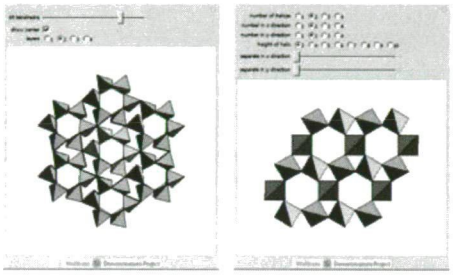

Fig. 1: (left): Expanding Tetrahedral Network - Tetrahedra are attached at their vertices in groups of six. **(right):** Helices of Tetrahedra - Tetrahedra are arranged along helices connected at vertices.

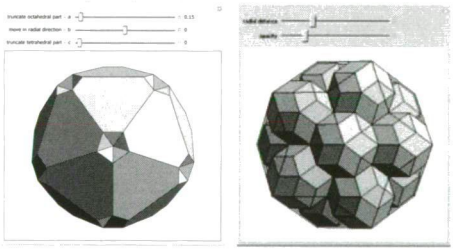

Fig. 2: (left): Boron suboxide - (chemical formula B60) is a solid compound of boron and oxygen. **(right):** Twelve rhombic triacontahedra are placed at the vertices of an icosahedron. Occur in quasicrystals

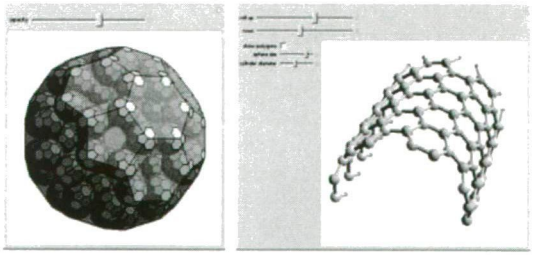

Fig. 3: (left): Buckyball of buckyballs. **(right):** Graphene. A planar hexagonal lattice is rolled up into a cylinder.

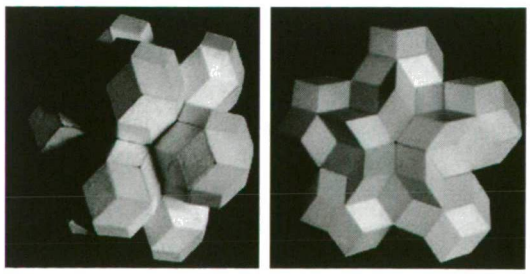

Fig. 4: Solid models.

IMACS: an international Master programme entirely devoted to clays

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Most existing Masters Courses dealing with clays focus on a single discipline or domain in which Clay Science does not necessarily constitute the main part of the course (Earth Sciences, Civil and Geotechnical Engineering, Materials Science, Environmental and Life Science, Chemistry and Chemical Engineering). However, Clay Science is a multidisciplinary endeavour, combining geology, mineralogy, crystallography, with physics, geotechnology, and soil mechanics together with inorganic, organic, physical and colloid chemistry and biochemistry. The IMACS (International Master in Advanced Clay Science) is the first multi-disciplinary programme that brings together the widely-distributed knowledge of clay science.

IMACS is an integrated 2 years master programme developed by five universities: the University of Poitiers (France), the Technical University of Crete (Chania - Greece), the University of Aveiro (Portugal), the University of Ottawa (Canada) and the Federal University of Rio Grande Do Sul (Porto Alegre – Brazil). AIPEA is an associated member of this consortium. The French Clay Group (GFA) also supports IMACS.

The teaching language is English. During the first year, basic knowledge on clays is provided, followed by a four month master project, which completes the first year programme. The second year incorporates two elective specialization options in the following fields: 1) Environment, soil and geological systems, 2) Geomaterials and civil engineering – Assessment and processing, 3) Advanced clay – nanomaterials, and 4) Healing minerals. The master thesis (6 months) completes this second year and can be carried out at any of the partner research laboratories. The completion of the curriculum is rewarded by a multiple Master Degree.

The IMACS programme was approved by the European Commission under a very competitive application scheme as an Erasmus Mundus Joint Master programme in July 2009 and it will open in September 2010. Erasmus Mundus is a cooperation and mobility programme in the field of higher education supported by the European Commission. This programme offers financial support for high-quality joint master courses, attractive scholarships/fellowships for both Non European and European student candidates and short-term scholarships for Non European and European academics to carry out research or teaching assignments as part of the joint masters project. Free language training in the local languages is offered by the five higher education institutions. Moreover, the programme makes available a range of services and facilities (e.g. visa request, accommodation, insurance, bank account opening, social and cultural activities among many others…) to the students.

This Masters Course is open to students holding a BSc (or a degree equivalent to 180 ECTS) or an academic equivalence based on professional experience, and a fluent understanding of the English language.

IMACS website: http://www.master-imacs.org

Teaching clay science and technology within a Geological Engineering Master program: Bologna Process implications

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Aveiro University (AU) was created in the mid-70's, establishing a Geosciences Department, the first in Portugal of its kind with the purpose of integrating the various areas regarding Sciences of the Earth, including the Engineering Science as well as the Geophysical Science. Teaching of clays and clay minerals deserve, since the beginning, particular attention in the Geological Engineering graduation program. Clay-related matters were teached within disciplines like Industrial Minerals, Ceramic Raw Materials and Crystallochemistry and Diffraction, but two very important steps were fulfilled first in 1986 with the inclusion, on the Geological Engineering graduation program, of a new discipline called Clays, entirely focused on clay science and technology, then in 1994 with the creation of the master degree in Industrial Minerals and Rocks (1994), offering clay formation within disciplines, such as Geology of Industrial Minerals, Exploration and Exploitation, Industrial Applications, Technologies, Mineral Economy.

The implementation of the Bologna process caused significant changes in the courses offered at AU. In the scope of Master Degrees, apart from the recreation of a master degree in Geological Engineering, the Department of Geosciences of the AU launched in conjunction with the Department of Geology of the Science Faculty of the University of Porto, a master degree in Geomaterials and Geological Resources, both offering several clay-related disciplines.

Recently, some advanced training courses (ATC), in which the Geosciences Department will play an important role, were put forward: (1) Strategies for the Protection of Lands, (2) Strategies for the Evaluation of contamination, (3) Rehabilitation of Lands; (4) Hydrogeophysics. The first three are strongly articulated among them and involve formation on clay science and technology. They are all related to fields of study aimed at an audience with a wide range of training in scientific and technological areas. The ATC does not confer degrees, but the approval in this type of training can be credited in other post-graduate, including doctoral programs.

ERASMUS IP: a simple and effective way for European teaching co-operations, the example of the ADVANCECLAY IP series (2008–2010)

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The Eötvös Loránd University (Budapest) has a long tradition in coordinating and hosting LLL ERASMUS Intensive Programmes (IPs) in the field of mineral sciences. The first IP took place in 2000 in Budapest, and since then, each year a 10-day international summer course was organized. Originally, the application and funding was coordinated from Brussels, but recently, applications have to be submitted in the host country of the IP. The application and the financial administration procedures of the ERASMUS IPs are relatively simple and they are really effective in enhancing international co-operations. In such training- and instrumentation-demanding fields like mineral sciences, IPs can further the usage of well equipped laboratories and fill up the gaps in university teaching programmes that originate from the lack of instrumentation.

We present our experience in the new, host country application system, through the ADVANCECLAY IP series, running in the years 2008–2010, in the hope to raise interest in organising similar events in other countries in the future. A specialty of the Hungarian IPs is that it is not only a tutorial event with lectures, practicals and labs, but students can present their results in the poster session and thus in a friendly environment they can experience how professional conferences work and how one shall prepare, and present a poster.

The ADVANCECLAY 1 IP took place in 18–29 July, 2008 in Budapest, on the topic "Dioctahedral Clay-Related Layer Silicates", with the participation of 23 teachers and 38 students, from 9 partner universities. It was the most classical summer school, with lectures, some practicals and a field trip.

The ADVANCECLAY 2 IP was held in 23 August – 2 September, 2009, in Budapest and Pécs (South Hungary), on the topic "Economic and Environmental Importance of Clays", with the participation of 13 teachers and 54 students, involving 6 partner universities. Here the emphasis was more laid on field activities: mine, factory and industrial plant visits.

The ADVANCECLAY 3 IP is scheduled for 27 August – 7 September, 2010, in Szeged, at the University of Szeged. The topic of the school is "Colloid Properties of Clays and Environmental Applications", with the participation of 63 students and 15 teachers, involving 11 partner universities. The main goal of the school is to amalgamate the mineralogical and chemical theoretical background of clay studies, with a large number of lab practicals.

Educational projects in Earth Sciences at University of Miskolc (Hungary)

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The Institute of Mineralogy and Geology, Faculty of Earth Science & Engineering has been coordinating several EU-co-funded educational projects. At the moment the Institute runs three projects of this kind.

The "EURO-AGES" (European Accredited Geological Study Programs) project aims at developing a qualification framework for geology, based on learning outcomes rather than input factors on the European level, thereby increasing transparency of the Earth Sciences qualifications and ultimately facilitating academic and professional mobility across Europe. The coordinator of the project is the ASIIN Consult GmbH Germany, the partners are from Belgium, Hungary, Spain and Sweden. The project moreover will provide important reference points for quality assurance and related recognition issues focused on learning outcomes. In this sense the project will add value to the implementation of the 2005 Directive on Recognition of Qualifications.

The project titled "Telkibánya Field Training Park" is being implemented in Hungarian-Slovakian cross-border cooperation. Telkibánya is a significant ancient mining town with outstanding medieval monuments of industrial history. In the frame of the project the partners create a joint field education centre in the area of the explored epithermal gold-silver mineralization. Besides setting up the infrastructural background, new teaching materials in English are worked out for field programs in geology, geophysics, mineralogy, geochemistry, ore exploration, mining, geotechnics and environmental engineering. Demo-courses for Hungarian and Slovakian participants at different levels (students at BSc, MSc, PhD, teachers of geography and environmental sciences, civil participants) are also organized as a part of the project. The training park is also offered as a scene for field programs for other universities as well.

The third project focuses on the development of teaching materials for the BSc program in Earth Science Engineering. The main aim is that beside the traditional contact hours, using multimedia tools, new, practice-oriented teaching materials are created for 16 courses in Hungarian and in English, which will be modern, on-line accessible and interactive. As the results of the project, the BSc in Earth Science Engineering program will be harmonized with the similar programs at other European universities, the international education facilities will be widened and the foreign job opportunities will be more favourable.

New approach in mineralogy and crystallography education by application of complex symmetry structures in old Eurasian ethnomathematics of Scythian, Xiongnu and Chinese archaeological finds of Ukraine, Russia, Mongolia and China

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The crystallographic structure of minerals can be described by the symmetries of the crystal lattice. Complex structures contain more than one space symmetry group for the arrangement of different atoms in their positions in the unit cell. For example in the garnet structure (pyrope) the AlO_6 octahedral and the SiO_4 tetrahedral units form a subsystem, and the position of the Mg atoms also can be given well visible in a coloured subsystem.

Over the classical group theoretical approaches there are other methods to help forming the spatial view and visuality of the students. Some technological structures triggered development of 2D complex crystallographic structures, which were discovered even in the 2500 years old Eurasian ornamental arts. Within this work, we collected several of them from the complex structures found on archaeological finds in royal tombs of Scythians (Kul Oba, Ukraine; Pazyryk, Russia), Xiongnu Huns (Noin Ula, Mongolia;) and Chinese (Urumchi and Mawangdui, China) (These studies are also called ethnomathematics).

This educational course uses both symmetry and cellular automata principles in forming the operations of complex patterns and structures (From symmetry to cellular automata). From friezes double friezes, woven 2D symmetry patterns and the two types of complex (composite) plane symmetry patterns are generated. Complex patterns of Coxeter-type [1], and Curie-type [2,3] are shown in archaeological finds. Coxeter-type colored groups of cm/pm and cmm/pmg occur at Pazyryk. The multilayered structures of Scythians (Kul Oba, cmm//pmm//cm) and Xiongnu Huns (Noin Ula, p4m//cm//p1) and Chinese (cmm//cm, Ürümchi) are the Curie-type variants. Even Curie-type multilayered structures with complex unification of four different patterns were found among the later steppe structures (Afrasiab, today Samarkand, Uzbeghistan) with p4m//cm//pm//pg structure.

Complex symmetry patterns help the spatial imagination and make more complete and vivid the rigid mathematical background, and also demonstrate that ancient masters of technologies were rich enough in intuitive structural knowledge to give ideas even for the recent time crystallographers.

[1] Coxeter, H.S.M. (1985) *Int. J. Quantum Chem.*, **31**, 455-461. [2] Curie, P. (1894) *J. Physique*, **3**, 393-415. [3] Bérczi, Sz. (2004) *Forma*, **19(3)**, 265-277, Tokyo.

Formal and non-formal learning about minerals and mineralogy. A case study

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Minerals have been precious materials for the development of civilizations and societies since the Prehistoric Times. First, the naturalists and the collectors, and then the Museums of Natural History have played an important role in the advancement and dissemination of Mineralogy. Moreover Museums have also been important as learning environments of Mineralogy. The purpose of this study is to present two examples of the teaching and learning of Mineralogy, considering the Mineralogy teaching experience at the Mineralogical and Geological Museum and at the Earth Sciences Department of the University of Coimbra in a non-formal and formal way respectively. A greater interest in minerals has been shown by teachers of Secondary Schools in the last decade. They often come to the Museum with their students. This interest may be related to the inclusion of the geological issues in the national curricula. Moreover, some scholars in the Department of Earth Sciences and in the Mineralogical and Geological Museum have developed some practical activities for the learning of minerals in a perspective of Education for sustainability in a non-formal way. These activities have been made to enable an active learning by participants, for example, by solving exercises and by handling minerals and rocks samples and everyday objects made from minerals. The participants, especially young boys and girls, aged 10 to 14, sometimes with their parents or their teachers, also have an opportunity to learn about minerals, as far as their classification, composition, diversity, occurrence, and use as a geological resource is concerned. Some activities also included the microscopic observation of minerals. Very often, the participants had a poor initial knowledge on these issues, but they developed good performances during activities and, ultimately, they evaluated them as important to very important [1]. Similar activities have also been developed within the framework of master courses for training teachers of Secondary Schools. In this case, materials for teaching minerals are being developed by master students who are attending the specific curricular units such as, Observation and Experimentation in Geosciences and Didactics of Geosciences II. In the last two years, 22 master students have made didactic materials to teach minerals in various perspectives, including the study of minerals as an important resource and the importance of minerals in the urban dust composition. At the end, these activities are significant not only because they contribute to the teacher training but also because they constitute potential activities to be developed in secondary schools in a classroom context or in the lab. Besides, school visits to the Museum are also an excellent opportunity to use these didactic materials. These two cases are examples of activities to promote learning about minerals and about their importance at different levels of education. We emphasize the learning and teaching minerals in a perspective of a *Sustainable Development*. These activities have been a success and they contribute to competence development of the participants, especially as far as the knowledge of mineralogy, geological resources and their uses and environmental implications is concerned. The promotion of these competences leads to a better understanding of minerals and to a greater discussion and participation performances.

[1] Gomes, C.R et al. (2009) *Enseñanza de las Ciencias*, Número Extra VIII Congreso Internacional sobre Investigación en Didáctica de las Ciencias, Barcelona, 2626-2629.

Joint European educational programs in mining, environmental and mineral sciences - Hungarian aspects

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The safe, sustainable and cost-efficient supply of primary and secondary raw materials is an indispensable base of a prosperous society. Against this background the European Geotechnical and Environmental Course (EGEC) as a part of the Erasmus Mundus Minerals and Environmental Programme (EMMEP) is a two-year MSc course to educate future managers and leaders in the European and worldwide mineral extractive industry. Other two coursef of the EMMEP are the European Mining Course (EMC) and the European Mineral Engineering Course (EMEC). The whole program is implemented by a consortium of six European universities with strong engineering background: TU Delft, University of Exeter (Camborne School of Mines), TU Helsinki, TU Wroclaw, University of Miskolc, and RWTH Aachen. The Erasmus mundus program leads to a double MSc degree in Minerals and Environmental Engineering. Students who complete the program have the advantage of excellent international employment opportunities.

The course is a two-year 120 ECTS programme in English. The consortium offers a unique curriculum with mineral resource and environmental courses in a combination which is not available at a single European institution. Entry requires a Bachelors' degree in natural resource engineering, or an equivalent discipline. The study plan comprises four semesters. Two semesters are reserved for an 8 months joint curriculum at 4 universities. The remaining two semesters are spent at the two universities awarding the double degree. Non-European candidates have the opportunity to get a scholarship from EU, which covers all their expenses during the four semesters.

The Faculty of Earth Science and Engineering, University of Miskolc takes part in the EGEC program. In 2010-2011 the following courses are offered: Environmental Risk Assessment, Environmental Bioprocessing, Environmental Geology and Environmental Geophysics (two month, 4 ETCS each). In the 3rd semester the students can study Groundwater Flow, Geotechnical Engineering, Engineering/Mining Geophysics, Mine Waste Geochemistry, Mineral Processing Tailings Management and Utilization, Numerical Methods in Geotechnics (four months, 5 ETCS each). In the last semester students have to take part in project works, and they should complete their thesis works.

Last year, in the frame of EGEC program there were participants from China, Chile, Namibia, Sierra Leone, Ethiopia, India, Pakistan, Iran, Nepal, and from a number of European countries, together with Hungarian students. In June 2010 the University of Miskolc and the Delft University of Technology awarded the master double degree in Miskolc for absolvents from Pakistan and Namibia.

The program is strongly supported by the industry (near 50 multinational firms, including the worldwide leading mining companies). The participating universities and the additional institutions and companies are in co-operation in the FEMP (Federation of European Mineral Programs). This has proven to be one of the most important factors of its success. A choice of internships and job opportunities are offered to participating EU and non-EU students. Further information is available at www.emmep.org

MINSPEC – the first Marie Curie Chair of Excellence in mineralogy (2006–2009)

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This contribution summarises the activities and impact of the Marie Curie Chair of Excellence for Mineral Spectroscopy (project no. MEXC–CT–2005–024878; acronym MINSPEC). It has made an outstanding contribution to the advanced-level teaching and training of mineralogy students, both in Vienna and on a European scale. This chair was established at the Institut für Mineralogie und Kristallographie, Universität Wien, Austria, for a three-year time period (April, 2006 – March, 2009). MINSPEC was the third Marie Curie Chair at all awarded to a host organisation in the country of Austria, and it was the first Europe-wide in the field of mineralogy.

In the framework of its Human Resources and Mobility (HRM) Activity, the European Commission funds, among others, a limited number (ca. 15/year) of temporary university chairs. The establishment of Marie Curie Chairs, part of the Marie Curie Excellence Promotion and Recognition program, aims at improving the university education in disciplines where the needs of an emerging research are not met by the existing, limited training opportunities. MINSPEC's main focus were mineralogical micro-spectroscopy techniques, in particular those that use light for sample excitation (i.e., Raman, infrared absorption, optical absorption, and photoluminescence).

The project's objectives have been accomplished convincingly. The host institute has strengthened its position as one of the internationally leading places for competent training in mineralogical light spectroscopy; an enormous amount of international recognition was gained. The dissemination of spectroscopy-related knowledge and data was improved, and it is being centralised by the chair's www pages (especially the "Spectroscopy Links"). The establishment of a European Centre for Mineral Spectroscopy at the host institute was initiated.

Activities included the training of graduates, Ph.D. students, and researchers; both at the host institute and at other institutions. One diploma and three Ph.D. projects were supervised by the chair-holder, and three more Ph.D. students from other countries were co-supervised during four-month periods which they spent at the host institute. On-site spectroscopy training was also provided to 28 short-term visitors (graduates, Ph.D. students, and researchers) from institutions in 13 countries. At the Universität Wien, the chair-holder taught 19 classes plus one field trip. In addition, three one-week short courses held at the host institute were organized, which overall gathered 94 participants (coming from 19 European countries, Russia, Israel, the U.S.A., Thailand, and Australia) and 15 invited international lecturers. External teaching and training was provided through lectures at universities in Germany, Slovakia, Slovenia, the United Kingdom, France, Spain, Greece, Norway, Russia, Thailand, and Australia; and a two-day short-course in Ljubljana, Slovenia, which was attended by 36 participants.

Associated was the research project "Micro-spectroscopy of radiation-damaged minerals". This and a broad range of additional research topics was dealt with, motivated by the goal to involve the supervised Ph.D. students in a large variety of analytical problems. Results led to important contributions to the understanding of radiation effects in minerals. Scientific co-operation with 51 institutions worldwide was conducted. Research results were presented in 20 papers in peer-reviewed journals (8 more were submitted by the time of the end of the project) and 34 conference presentations, five of which were invited. The Universität Wien has finally decided to maintain the chair beyond the temporary EU funding period, as permanent full professorship for mineralogy and spectroscopy.

Paleoenvironmental controls on clay mineralogy of Carnian sections from the Transdanubian Central Range, Hungary

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Clay mineralogy is considered to be a powerful tool for interpretation of weathering conditions and paleoclimate in the source area. In general, illite and chlorite have been considered to be less sensitive to chemical weathering and may be used as internal standards or comparators, hence the kaolinite/illite and/or smectite/illite ratios are used by many authors as paleoclimate proxies. The abundance of kaolinite is especially a good indicator of landmasses with hot and humid (subtropical to tropical) climate supported by high water/rock ratio and steep slopes with good drainage. Smectite is generally suggested to form during weathering in seasonally wet and dry climates with low water/rock ratio and lower slopes, and low relief with poor drainage.

The Upper Triassic sediments both in NW Europe and in the Mediterranean show evidences for a generally arid climate regime. However, in the Carnian, a biotic crisis, extinction event, oceanographic changes, increased rainfall and an anomalous siliciclastic input to the oceanic basins occurred contemporaneously at this time, which interrupted the warm and arid climatic conditions. The paleoclimatic and paleo-environmental interpretation of the changes recorded by Carnian successions in Europe remain controversial.

The Carnian marine succession of Veszprém Marl and Sándorhegy Formations from the Transdanubian Central Range (Hungary) shows significant change in sedimentation: pelagic carbonate deposition was replaced by formation of fine-grained marly sediments. The clay mineralogical composition of 240 samples four boreholes (Bszü-1, Bfü-1, Met-1, and Zs-14) was determined by XRD analysis in order to model the paleoenvironment.

The clay fraction of the samples includes variable proportions of illite, illite/smectite mixed-layer minerals (IS), chlorite, and kaolinite. High degree of expandability (50–70%) and poorly ordered character (S=0) of the IS resulted from relatively low degree of diagenetic overprint. Therefore, the clay mineralogical composition seems to be an original signal applicable to reconstruct the paleoenvironment. The relatively large amount of detrital illite (~40–60%) and chlorite (~10–30%) associated with kaolinite (~10–20%) reflects strong erosion of high relief areas and increased rate of continental weathering. The IS (up to ~60%) can be formed from smectite via burial diagenesis and the originally smectitic material could be derived from altered volcanogenic rocks. Carbonate-rich intervals are enriched in IS whereas marl-dominated intervals are richer in illite which was caused either by fluctuations of terrigenous input or sea-level fluctuations. Based on these results, mixed carbonate-siliciclastic basinal sediments representing the 'Carnian Pluvial Event' in the Transdanubian Central Range could be a superimposed product of climatic change, sea-level variation and tectonism.

AUTHORS' INDEX

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INSTRUCTIONS FOR AUTHORS

General

Acta Mineralogica-Petrographica (AMP) publishes articles (papers longer than 4 printed pages but shorter than 16 pages, including figures and tables), notes (not longer than 4 pages, including figures and tables), and short communications (book reviews, short scientific notices, current research projects, comments on formerly published papers, and necrologies of 1 printed page) dealing with crystallography, mineralogy, ore deposits, petrology, volcanology, geochemistry and other applied topics related to the environment and archaeometry. Articles longer than the given extent can be published only with the prior agreement of the editorial board.

In the form of two subseries, AMP publishes materials of conferences (AMP Abstract Series) and field guides (AMP Field Guide Series), or, occasionally supplement issues related to other scientific events.

The journal accepts papers that represent new and original scientific results, which have not appeared elsewhere before, and are not in press either.

All articles and notes submitted to AMP are reviewed by two referees (short communications will be reviewed only by one referee) and are normally published in the order of acceptance, however, higher priority may be given to Hungarian researches and results coming from the Alpine-Carpathian-Dinaric region. Of course, the editorial board does accept papers dealing with other regions as well, let they be compiled either by Hungarian or foreign authors.

The manuscripts (prepared in harmony of the instructions below) must be submitted to the Editorial Office in triplicate. All pages must carry the author's name, and must be numbered. At this stage (revision), original illustrations and photographs are not required, though, quality copies are needed. It is favourable, if printable manuscripts are sent on disk, as well. In these cases the use of Microsoft Word or any other IBM compatible editing programmes is suggested.

Language

The language of AMP is English.

Preparation of the Manuscript

The different parts of the manuscript need to meet the instructions below:

Title

The title has to be short and informative. No subtitles if possible. If the main title is too long, an additional shortened title is needed for the running head.

Author

The front page has to carry (under the main title) the full name(s) (forename, surname), affiliation(s), current address(es), e-mail address(es) of the author(s).

Abstract and keywords

The abstract is required to be brief (max. 250 words), and has to highlight the aims and the results of the article. The abstracts of notes are alike (but max. 120 words). As far as possible, citations have to be avoided.

The abstract has to be followed by 4 to 10 keywords.

Text and citations

The format of the manuscripts is required to be: double-spacing (same for the abstract), text only on one side of the page, size 12 Times New Roman fonts. Margin width is 2.5 cm, except the left margin, which has to be 3.5 cm wide. Underlines and highlights ought not be used. Please avoid the use of foot and end notes. Accents of Romanian, Slovakian, Czech, Croatian etc. characters must be marked on the manuscript clearly.

When compiling the paper an Introduction – Geological setting – Materials and Methods – Results – Conlclusions structure is suggested.

The form of citations is: the author's surname followed by the date of publication e.g. (Szederkényi, 1996). In case of two authors: (Rosso and Bodnar, 1995) If there are more than two authors, after the first name the co-authors must be denoted as "et al.", e.g. (Roser et al., 1980).

References

The reference list can only consist of published papers, M.Sc., Ph.D. and D.Sc. theses, and papers in press.

Only works cited previously in the text can be put in the reference list. Examples:

Best, M.G., Christiansen, E.H. (eds.) (2001): Igneous petrology. Blackwell, Edinburgh, 458p.

Upton, B.G.J., Emeleus, C.H. (1987): Mid-Proterozoic alkaline magmatism in southern Greenland: the Gardar province. In: Fitton, J.G., Upton, B.G.J. (eds.): Alkaline Igneous Rocks. Blackwell, Edinburgh, 449–472.

Rosso, K.M., Bodnar, R.J. (1995): Microthermometric and Raman spectroscopic detection limits of CO_2 in fluid inclusions and the Raman spectroscopic characterization of CO_2. Geochimica et Cosmochimica Acta, **59**, 3961-3975.

Szederkényi, T. (1996): Metamorphic formations and their correlation in the Hungarian part of Tisia Megaunit (Tisia Megaunit Terrane). Acta Mineralogica-Petrographica, **37**, 143-160.

Bakker, R.J. (2002): http://www.unileoben.ac.at/~buero62/minpet/Ronald/Programs/Computer.html. Accessed: June 15, 2003.

The full titles of journals ought to be given. In case more works of the same author are published in the same year, then these has to be differentiated by using a, b, etc. after the date.

Illustrations

Finally, each figure, map, photograph, drawing, table has to be attached in three copies, they must be numbered and carry the name of the author on their reverse. All the illustrations ought to be printed on separate sheets, captions as well if possible. Foldout tables and maps are not accepted. In case an illustration is not presented in digital form then one of the copies has to be submitted as glossy photographic print suitable for direct reproduction. Photographs must be clear and sharp. The other two copies of the illustrations can be quality reproductions. Coloured figure, map or photograph can only be published at the expense of the author(s).

The width of the illustrations can be 56, 87, 118, or 180 mm. The maximum height is 240 mm (with caption).

All figures, maps, photographs and tables are placed in the text, hence, it is favourable if in case of whole page illustrations enough space is left on the bottom for inserting captions. In the final form the size of the fonts on the illustrations must be at least 1,5 mm, their outline must be 0,1 mm wide. Digital documents should be submitted in JPG-format. The resolution of line-drawings must be 400 dpi, while that of photographs must be 600 dpi. The use of Corel Draw for preparing figures is highly appreciated, and in this case please submit the .CDR file, as well.

Proofs and Offprints

After revision the author(s) receive only the page-proof. The accepted and revised manuscripts need to be returned to the Editors either on disc, CD or as an e-mail attachment. Proofreading must be limited to the correction of typographical errors. If an illustration cannot be presented in digital form, it must be submitted as a high quality camera-ready print.

The author(s) will receive 25 free offprints. On payment of the full price, further offprints can be ordered when the corrected proofs are sent back.

Manuscripts for publication in the AMP should be submitted to:

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